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Calculation of acid dissociation constants

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Calculation of acid dissociation constants

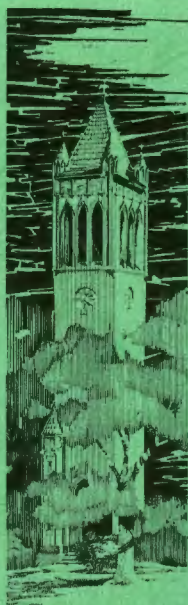
Abstract

A computational method has been developed for the determination of dissociation constants of acids (and bases). The method is applicable to mono or polybasic acids and, in certain cases, to mixtures of acids. A least-squares treatment is employed, and no simplifying assumptions are made in any of the equations or factors involved. All the available data are utilized, and provision is made for including or calculating activity coefficients. Utilization of the method requires a medium to large size digital computer.

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CALCULATION OF ACID DISSOCIATION
CONSTANTS

by

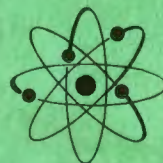
Wayne Woodson Dunning and Don S. Martin

PHYSICAL SCIENCES READING ROOM

AMES LABORATORY

RESEARCH AND
DEVELOPMENT
REPORT

U.S.A.E.C.



IS-822

Chemistry (UC-4)
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UNITED STATES ATOMIC ENERGY COMMISSION

Research and Development Report

CALCULATION OF ACID DISSOCIATION
CONSTANTS

by

Wayne Woodson Dunning and Don S. Martin

February, 1964

Ames Laboratory
at
Iowa State University of Science and Technology
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IS-822

CALCULATION OF ACID DISSOCIATION CONSTANTS*

Wayne Woodson Dunning and Don S. Martin

ABSTRACT

A computational method has been developed for the determination of dissociation constants of acids (and bases). The method is applicable to mono or polybasic acids and, in certain cases, to mixtures of acids. A least-squares treatment is employed, and no simplifying assumptions are made in any of the equations or factors involved. All the available data are utilized, and provision is made for including or calculating activity coefficients. Utilization of the method requires a medium to large size digital computer.

The resolution of successive dissociation constants of small ratio has been shown to present no difficulties attributable to such ratios; ratios as small as three were resolved as readily as those much larger. The accuracy attainable depends entirely upon the accuracy of the titration data. Tests have shown that titrations accurate to better than one part in five thousand may still produce two percent errors in the resulting constants. Consistent or random titration errors are likely to cause considerable variations in the dissociation constants. Experimental work must be performed with the greatest care if constants of even two significant figures are desired. Ordinary pH titrations may give uncertainties in even the first figure.

Mixtures of acids proved to be no more difficult to resolve than single acids, within certain severe limits. If there is a considerable separation in constants, and the data are extremely accurate, useful results may be obtained. In most cases, overlap of constants and/or experimental errors will prevent successful resolution.

Many previous methods of calculating dissociation constants have treated polybasic acids as mixtures of monobasic acids. It has been shown that if the ratio of successive constants is one hundred or more, no appreciable error results. With the present method, however, such assumptions are completely unnecessary.

Examination of the literature, together with experimental results obtained in this work, indicates that many "accepted" values are either very inaccurate, or at least given to more significant figures than justified.

* This report is based on a Ph. D. thesis submitted by Wayne Woodson Dunning, February, 1964, to Iowa State University, Ames, Iowa.

I. INTRODUCTION

The determination of the dissociation constants of acids¹ -- though sometimes considered to be a very straightforward procedure -- entails in practice numerous experimental and theoretical difficulties. The variety of experimental methods that have been used, the corrections applied to the data, the numerous manners in which data for identical procedures have been treated, and the considerable disagreement in values of the dissociation constants obtained are all indicative of the difficulties. The research reported in this work was undertaken primarily for the purpose of developing computational methods that would furnish the best possible values of dissociation constants from the data of any of several different experimental procedures.

A. Experimental Background

Among the many experimental procedures used in the past, one of the most common was the measurement of the conductance of an aqueous solution of the acid. This method was used primarily on monobasic acids, since polybasic acids presented great mathematical difficulties. As late as 1959, Dippy et al. (1) expressed the opinion that there was still no wholly satisfactory method of calculating the second and higher thermo-

¹Although this work deals specifically with acids, the treatment of bases is quite analogous, and the necessary modifications to the theoretical equations and the computer program are included.

dynamic dissociation constants of polybasic acids from conductivity data. Conductance methods are now considered obsolete by some authorities (2).

Another common procedure, and one which still sees extensive use, is that of optical measurement. This may be either colorimetric or spectrophotometric. The colorimetric method enables one to obtain a pH titration curve while avoiding some of the problems arising in standard electrometric determinations. However, standards of known dissociation constant are necessary for calibration of the indicators, and this can give rise to other difficulties. Spectrophotometric methods are quite useful in many cases, though extensive computations, similar in principle to those employed in this work, are often required.

Among the other methods or measurements that have been employed at one time or another for the determination of dissociation constants are: a) the change in freezing point; b) hydrolysis of salts (3); c) catalytic effect on the rates of sugar inversion (4); d) solubility of slightly soluble acids in solutions of salts of other acids (5); and e) kinetic methods.

Perhaps the most common procedure, in both past and present use, for determining dissociation constants is that of electrometric measurement. It has long been recognized that the measurement of the change in pH during the neutralization

of a weak acid with a strong base can be employed to obtain an accurate value for the concentration of the acid and its dissociation constant(s). In an electrometric titration, the pH values are measured at successive steps in the titration by means of the changing potentials of suitable electrodes immersed in the solution. According to usual practice, successive portions of a solution of strong base are added to a sample of pure acid and the pH values of the several mixtures are determined.¹ The titration is performed in a vessel that contains a hydrogen, glass, or quinhydrone electrode, and the cell system is completed by a reference half-cell (calomel, AgCl, etc.) whose electrolyte is brought into liquid-liquid contact with the acid solution in the titration vessel.

The pH values derived from the e.m.f. measurements of such a cell often involve considerable uncertainty, and in unfavorable cases they may be in error by more than 0.05 pH units (6). A principle reason for this difficulty is the neglect of the contribution of the potential of the liquid junction or in the application of improper or inadequate corrections. Such corrections are laborious and unsatisfactory, and require a knowledge, often unavailable, of the mobilities and activities of the ions of which the solutions are composed.

¹Numerous variations are possible, and under certain conditions may be more practical. The computational methods developed in this work are designed to accommodate some of the variations.

It has been shown (7) that partial corrections may produce a larger error than no corrections at all. Therefore, for accurate work, liquid junctions are to be avoided whenever possible. For approximate work, however, cells with liquid junctions are often useful.

A second limitation to the accuracy of these titrations has its origin in the changing concentration of ionized solutes in the vessel during the titration. A solution of a weak acid has a low ionic strength, whereas its salt is a strong electrolyte. There is no unique titration curve for a weak acid; it is well known that the curve is affected by the ionic strength of the solution. Several procedures are available for resolving this difficulty. One can make 1) a series of pH measurements of buffered solutions at varying ionic strengths, with extrapolation to zero ionic strength; 2) a series of titrations at varying ionic strength, with extrapolation to zero, or 3) a titration with corrections for ionic strength at each point by means of the Debye-Huckel equation

$$-\log f_i = \frac{A z_i^2 \sqrt{\mu}}{1 + B a_i \sqrt{\mu}} - \beta \mu \quad 1$$

where f_i is the activity coefficient, z_i is the valence of the ion i , a_i is the average effective diameter of the ion in Angstroms, β is an empirical coefficient dependent upon the system under study, and A and B are coefficients whose values vary with the temperature and dielectric constant of the

solvent. The ionic strength, μ , is defined by Lewis and Randall (8) as

$$\mu = \frac{1}{2} \sum m_i z_i^2 \quad 2$$

where m_i is the molal concentration of ion i .¹

The lack of a completely standardized scale of pH may lead to further problems, particularly in the re-evaluation of older data. The simple hydrogen ion concentration

$$\text{pCH} = -\log c_H \quad 3$$

$$\text{or} \quad \text{pCH} = -\log m_H \quad 3a$$

is used in much of the older literature, and great care must be taken when recalculating data from such work, if one wishes to obtain meaningful answers.

The Sorensen scale is a conventional one², defined in terms of the potential of the cell Pt;H₂,Soln. X/Salt bridge/0.1 N Calomel electrode,

$$\text{pSH} = \frac{E - 0.3376}{0.05916} \quad \text{at } 25^\circ, \quad 4$$

It is a measure of neither concentration, nor activity of the

¹The standard state of unit activity coefficient at infinite dilution requires that activity on the scales of volume concentration (c) and molality (m) shall be related by $a_c = a_m d^0$, where d^0 is the density of water. At 25° or less, this difference is negligible and will be ignored in this work.

²A conventional scale is one in which the values of a_H , although not truly hydrogen ion activities, will nonetheless be numbers which, inserted in equations involving a_H , will furnish results consistent with those obtained by rigorous thermodynamic methods.

hydrogen ion. In spite of this fact that psH bears no simple direct relationship to chemical equilibria, this scale has been widely used, and extensive tables of psH values for buffer mixtures are available (9).

The recognition that the e.m.f. of galvanic cells reveals changes of activity rather than of concentration, brought about the proposal by Sorensen and Linderstrom-Lang (10) of a new pH unit

$$\text{paH} = -\log a_{\text{H}} = -\log (f_{\text{H}}c_{\text{H}}) \quad 5$$

where a_{H} is the activity, and f_{H} the activity coefficient corresponding to the scale of concentration. The fact that the activity of a single ionic species is a concept lacking unique physical definition does not preclude the establishment of a reasonable scale of paH , but this scale must be a conventional one.

Guggenheim (11) and Hitchcock (12) have called attention to the advantages of a unit of acidity defined as

$$\text{pWH} = -\log (f_{\text{H}}f_{\text{Cl}}m_{\text{H}}) \quad 6$$

Unlike paH , this quantity is physically defined at all ionic strengths, and can be determined exactly from measurements of cells without liquid junction comprising electrodes reversible to hydrogen and chloride ions.

Since pWH is therefore a quite useful concept, it is fortunate that conversion can be made between it and paH with sufficient accuracy for most purposes, provided that the

ionic strength is not too high.

The common "pH meter" employing a glass electrode enjoys widespread popularity, and it is worthwhile to note that the development of pH standards allows one, without the necessity of liquid junction corrections, to make determinations of what is essentially p_aH , but only under certain specific conditions. It is safe to say that no quantitative interpretation of measured pH values should be attempted unless the medium can be classified as a dilute aqueous solution of simple solutes. This requirement excludes all non-aqueous media, suspensions, colloids, and aqueous solutions of ionic strengths greater than 0.2. From this point of view, the "ideal" solutions are those which match the standards of reference, namely aqueous solutions of buffers and simple salts with ionic strengths between 0.01 and 0.1. Under these very restricted conditions, the measured pH may be expected to approach an experimental $-\log f_H^m$, where f_H is defined in a conventional manner consistent with the assignment of the pH values of the standards with which the instrument was adjusted. For all practical purposes, the value of f_H in this dilute range is given by equation 1 with a_i values of 4 to 6.

B. Computational Methods

The number of mathematical treatments that have been applied to electrometric or pH titration data may well be larger

than the number of experimental procedures devised for determining dissociation constants. A thorough analysis of them is not practicable in this work, but a brief discussion of some of the methods will be given.

A simple approximation -- one that has been in use for more than fifty years (13) -- is that $K = [H^+]$ at the one-half neutralization point of a monobasic acid. This is, of course, not strictly true, and has the further disadvantage of making the value of the dissociation constant dependent upon only one pH determination.

Auerbach and Smolczyk (14) proposed a set of theoretical equations involving some assumptions which were shown by Britton (15) to be erroneous. Nonetheless, these equations have been widely used. The final values of dissociation constants obtained by this treatment are generally the averages of constants calculated from various combinations of the titration points.¹

A logarithmic equation was derived by Cohn et al. (16) but does not appear to have seen any further use. It is apparently limited to monobasic acids.

¹This method of "using all the data" is apparently still popular. It is generally applied in a rather random fashion, as there is no known formal procedure for its use. The process is essentially one of averaging, and is not generally considered to have the merit of the least-squares method.

Several workers have developed equations by means of which a polybasic acid is treated as a mixture of monobasic acids. The "titration constants" thus obtained are presumably convertible to the true dissociation constants by means of simple relationships. This approach has apparently not seen extensive use, despite its multiple development.

Speakman (17) devised an approach that appears to have considerable merit, although it is in general limited to dibasic acids. The data, modified by the appropriate equations, are recorded graphically, and an essentially linear plot is obtained. The slope of the line gives K_1 , and the intercept gives K_1K_2 . Drawing the "best" straight line is considered to give the best use of all the data. Speakman considers extrapolation to zero ionic strength to be inferior to making proper activity corrections at finite ionic strength.

The general treatment of polybasic acid titration curves has been a matter of much study and many suggestions. So far as is known, this work presents the first completely general treatment of such situations. Previously, it was common to develop specific data treatments for varying situations, depending largely upon the ratio(s) of the several dissociation constants. Where this ratio is over 500 to 1000, the acid was generally treated as a mixture of monobasic acids. As the ratio decreased, various approximations were necessary, graphical treatment might be required, etc. In at least one

study, equations were developed for five different cases, none of the treatments being exact. It is the intention of this work to present a treatment that is applicable to mono- or polybasic acids, or to mixtures of acids under certain conditions, which makes no simplifying assumptions for any case, and which utilizes all the data for any of several types of titrations. The method of least-squares is employed, and an estimate of the errors in the individual constants is obtained.

II. EXPERIMENTAL

A. Materials

1. Acids

Standard commercial reagents, in grades meeting A. C. S. specifications, were used without further purification.

2. Base

A stock solution of sodium hydroxide was prepared by the dilution of a filtered, concentrated solution of the reagent grade chemical. It was standardized against potassium biphthalate by potentiometric titration.

3. Buffer

Primary standard grade potassium biphthalate was used to standardize the pH meter for all titrations. A 0.05 M solution has a pH of 4.01 at 25°.

4. Water

Tap distilled water was redistilled from alkaline permanganate solution for use in all preparations and titrations.

B. Equipment

A Beckman model "G" pH meter was used in all pH determinations. Shielded electrodes, model 1190-80, permitted pH determinations outside the shielded cabinet. No electrode corrections were applied to any readings.

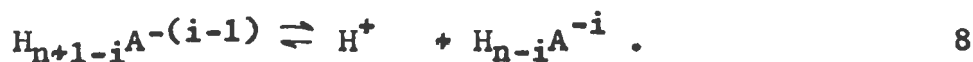
III. MATHEMATICAL THEORY

A. Titration of a Single Acid

The simplified chemical equation for the dissociation of an acid, represented by the formula H_nA , in water or other suitable solvent is



or, for the i^{th} step of the reaction, where i varies from one to n ,



The general equation for the thermodynamic dissociation constants of the acid is

$$K_i = \frac{[H_{n-1}A^{-i}] \gamma_i (H^+)}{[H_{n+1-i}A^{-(i-1)}] \gamma_{i-1}} \quad 9$$

where the brackets represent ionic concentrations, and the parentheses represent ionic activities. The γ_i are the activity coefficients for the ions of charge $-i$; since uncharged species are considered to be of unit activity, $\gamma_0 = 1$.

Equation 9 may be rearranged to

$$[H_{n-i}A^{-i}] = K_i \frac{\gamma_{i-1}}{\gamma_i} \frac{[H_{n+1-i}A^{-(i-1)}]}{(H^+)} \quad 10$$

and proper substitution of successive terms will give

$$[H_{n-i}A^{-i}] = \frac{\gamma_0}{\gamma_i} \frac{[H_nA]}{(H^+)^i} \prod_{i=1}^i K_i \quad 11$$

Since the products of the dissociation constants will be encountered so frequently, it is useful to define

$$k_i = \prod_{q=1}^i K_q \quad 12$$

and

$$k_0 = 1. \quad 13$$

The total concentration of the acid, C_a , is the sum of the concentrations of the unionized molecule and all the ionized species, and may be expressed as

$$C_a = [H_nA] \left(1 + \sum_{i=1}^n \frac{k_i}{\gamma_i (H^+)^i} \right). \quad 14$$

For ionic balance in solution, it is necessary that the following condition be met:

$$[H^+] + [Na^+] = [OH^-] + [Cl^-] + \sum_{i=1}^n i[H_{n-1}A^{-i}] \quad 15$$

where $[Na^+]$ is usually due to the base added, and $[Cl^-] = 0$. If the salt of an acid is being titrated with a strong acid, then $[Na^+]$ is equal to the salt concentration, and $[Cl^-]$ is due to the acid added.

The equations may be simplified somewhat by making the convenient definition

$$N = [H^+] + [Na^+] - [OH^-] - [Cl^-] \quad 16$$

or, in terms including activities, activity coefficients, and the dissociation constant of water,

$$N = \frac{(H^+)}{\gamma_H} + [Na^+] - \frac{K_w}{(H^+) \gamma_{OH}} - [Cl^-]. \quad 17$$

Combination of Equations 15 and 16 gives

$$N = \sum_{i=1}^n i [H_{n-i} A^{-i}] \quad 18$$

and from Equations 11, 12 and 14, one finds that

$$N = \left(\sum_{i=1}^n \frac{iki}{\gamma_i (H^+)^i} \right) \left(\frac{Ca}{1 + \sum_{i=1}^n \frac{k_i}{\gamma_i (H^+)^i}} \right) . \quad 19$$

Multiplication of this by $(H^+)^n / (H^+)^n$ gives

$$N = \left(\sum_{i=1}^n \frac{iki (H^+)^{n-i}}{\gamma_i} \right) \left(\frac{Ca}{(H^+)^n + \sum_{i=1}^n \frac{k_i (H^+)^{n-i}}{\gamma_i}} \right) . \quad 20$$

Rearrangement of terms gives

$$N \left[(H^+)^n + \sum_{i=1}^n \frac{k_i (H^+)^{n-i}}{\gamma_i} \right] = \sum_{i=1}^n \frac{iki (H^+)^{n-i} Ca}{\gamma_i} \quad 21$$

and the separation and recombination of terms gives

$$N(H^+)^n = \sum_{i=1}^n k_i \left(\frac{i Ca - N}{\gamma_i} \right) (H^+)^{n-i} . \quad 22$$

There is one such equation for each data point, resulting in a set of equations in n unknowns for a given titration. There will most generally be more than n data points, and in order that the best possible use may be made of all the experimental data for a titration, the method of least-squares, or multiple regression, is employed in solving the set of equations.

The particular treatment used in this work may be best

illustrated by simplifying the coefficients of Equation 22 to give

$$Y = A_1 k_1 + A_2 k_2 + \text{-----} A_n k_n \quad . \quad 23$$

The coefficients of the numerous individual equations are multiplied and summed to form the following set of equations:

$$\begin{aligned} (\sum A_1 Y) &= (\sum A_1 A_1) k_1 + \text{-----} (\sum A_1 A_n) k_n & 24 \\ \vdots & \quad \quad \quad \vdots \\ (\sum A_n Y) &= (\sum A_n A_1) k_1 + \text{-----} (\sum A_n A_n) k_n \quad . \end{aligned}$$

This set may be solved for the k_i by any of several standard methods. The dissociation constants, K_i , are then obtained from an equation analogous to Equation 12.

$$K_i = \frac{k_i}{k_{i-1}} \quad . \quad 25$$

B. Mixture of Two Acids

The addition of a second acid, $H_m B$, to the system introduces certain complications. Dissociation constants for the second acid are K_j , and the equations which differ significantly from those for a single acid are

$$k_j = \prod_{j=1}^j K_j \quad , \quad 26$$

$$N = \sum_{i=1}^n i [H_{n-i} A^{-i}] + \sum_{j=1}^m j [H_{m-j} B^{-j}] \quad 27$$

and

$$N = \left(\sum_{i=1}^n \frac{ik_i (H^+)^{n-i}}{\gamma_i} \right) \left(\frac{C_a}{(H^+)^n + \sum_{i=1}^n \frac{k_i (H^+)^{n-i}}{\gamma_i}} \right) +$$

$$\left(\sum_{j=1}^m \frac{jk_j (H^+)^{m-j}}{\gamma_j} \right) \left(\frac{C_b}{(H^+)^m + \sum_{j=1}^m \frac{k_j (H^+)^{m-j}}{\gamma_j}} \right). \quad 28$$

This equation may be reduced to

$$N(H^+)^{n+m} = \sum_{i=1}^n k_i \left(\frac{i C_a - N}{\gamma_i} \right) (H^+)^{n+m-i} +$$

$$\sum_{j=1}^m k_j \left(\frac{j C_b - N}{\gamma_j} \right) (H^+)^{n+m-j} +$$

$$\sum_{i=1}^n \sum_{j=1}^m k_i k_j \left(\frac{i C_a + j C_b - N}{\gamma_i \gamma_j} \right) (H^+)^{n+m-i-j}. \quad 29$$

A non-linear method must be employed in the solution of this system due to the fact that products of the variables are present. So far as is known, all methods for solving non-linear systems of equations on digital computers are iterative and have one of two disadvantages: either reasonably good initial estimates of the variables are required to assure convergence, or else the equations are expanded at each iteration and the program may bog down of sheer complexity. In this work, the Newton-Raphson method of iteration, as employed by Crosbie and Monahan (18), was chosen as the most suitable and convenient.

The method of least-squares requires the minimization of Q in the equation

$$Q = \sum (Y_C - Y_M)^2 \quad 30$$

where

$$Y = N(H^+)^{n+m} \quad 31$$

and may be either a measured value, Y_M , by virtue of Equation 16, or a calculated value, Y_C , from Equation 29 and the estimates of the $k_{i,j}$.

The appropriate corrections, (\vec{dk}) , in vector notation, to the variables would result in

$$Q + \sum \left(\frac{\partial Q}{\partial k} \right) (\vec{dk}) = 0. \quad 32$$

From this, it follows that

$$\sum \left(\frac{\partial Q}{\partial k} \right) (\vec{dk}) = -Q \quad 33$$

and

$$\sum \left(\frac{\partial Q}{\partial k} \right) = \sum 2(Y_C - Y_M) \left(\frac{\partial Y_C}{\partial k} \right) \quad 34$$

Therefore

$$\sum 2(Y_C - Y_M) \left(\frac{\partial Y_C}{\partial k} \right) (\vec{dk}) = \sum -(Y_C - Y_M)^2 \quad 35$$

or

$$\sum 2 \left(\frac{\partial Y_C}{\partial k} \right) (\vec{dk}) = \sum (Y_M - Y_C). \quad 36$$

This can be most conveniently solved by multiplying by $(\partial Y_C / \partial k)$ and expressing the entire equation in vector or matrix notation,

$$\left[\sum_{1=1}^{ND} \sum_{a=1}^{n+m} \left(\frac{\partial Y_C(1)}{\partial k_a} \right)^2 \right] [dk] = \left[\sum_{1=1}^{ND} \sum_{a=1}^{n+m} (Y_M(1) - Y_C(1)) \left(\frac{\partial Y_C(1)}{\partial k_a} \right) \right] \quad 37$$

where ND is the number of points on the titration curve.

This system,

$$[G][dk] = [R] \quad 38$$

is solved for the vector $[dk]$ by matrix inversion to yield improved values of the variables, $k_a = k_a^0 + d k_a$.

C. Modified Titrations

The principal variation that will be encountered is probably the titration of a weak base with a strong acid. In addition, the free acid (or base) may occasionally be unobtainable, necessitating the titration of a sodium or potassium salt of the acid with strong acid. Fortunately, modifications to the equations already developed are either slight or unnecessary and the changes in computer programming required to handle all four situations are minor.

1. Salt of weak acid titrated with strong acid

The only changes needed are that $[Na^+]$ be made equal to the salt concentration, and $[Cl^-]$ is now the concentration of the acid titrant.

2. Weak base titrated with strong acid

For the titration of a base, $M(OH)_n$, with acid, Equation 18 is changed to

$$N = \sum_{i=1}^n i[M(OH)_{n-i}^{+i}] \quad 39$$

Equation 16 remains the same, except for a change in sign, since N will now represent the total concentration of all simple negative ions. The value of $[\text{Na}^+]$ will generally be zero, and $[\text{Cl}^-]$ will be the concentration of the acid titrant.

3. Salt of weak base titrated with strong base

This case is very similar to that of Section 1 above. $[\text{Cl}^-]$ equals the salt concentration, and $[\text{Na}^+]$ is the concentration of the base titrant. The quantity N has the same sign as in Section 2.

D. Calculation of Titration Curves

It is sometimes useful to calculate an exact titration curve from known dissociation constants and concentrations.

An iterative process is necessary for curve calculation, due to the continual corrections for volume change. The required sodium ion concentration (or chloride ion, depending upon the type of titration) at each desired pH on the titration curve is calculated from Equation 19 and 16. The previous value of $[\text{Na}^+]$ is obtained from the expression

$$[\text{Na}^+] = \frac{\text{Total volume of base added}}{\text{Total volume of solution}} \times \text{base normality.} \quad 40$$

The difference, required $[\text{Na}^+] - \text{Previous } [\text{Na}^+]$, is multiplied by the total solution volume and divided by the concentration of the base to obtain the volume of base that must be added.

This calculated amount is added to the solution, and then a test is made to determine whether or not sufficient accuracy has been achieved. Generally, if the amount of base added (or subtracted, since the quantity may have either sign) is less than 0.001 ml, no further adjustments are made to the particular point on the curve in question.

E. Calculation of Acid Concentrations

The concentration of an acid can be readily obtained from its titration curve and dissociation constants by means of Equations 20 or 28 and the linear least-squares treatment. For a single acid, this is of doubtful utility since standard analytical analysis of the titration curve will generally give a value of completely satisfactory accuracy. For a mixture of acids, however, this calculation may be of some importance as there may be no break in the curve.

F. Determination of Errors

The method of least-squares can be reasonably depended upon to do a good job of fitting a particular equation to a given set of data. It does not, however, necessarily indicate how well the answers obtained satisfy the equation and data. It is therefore highly advantageous to determine the standard deviations of the final results; these will give indications of the random errors in the data, or perhaps evidence that the

chosen equation was not the proper one. In the latter case, this would be due to improper choice of the initial parameters specifying the number of acids or dissociation constants.

In all cases in this work, the same procedure is used to obtain the standard deviations of the particular results. The systems of linear equations are solved by the method for non-linear equations on the last iteration. The diagonal elements of the inverse matrix G^{-1} , from Equation 38, are transformed into the standard deviations by the expression

$$(\sigma_{R_L})^2 = \frac{G^{-1}(L,L) \times Q}{ND-NC-1} \quad 41$$

where ND is the number of points on the titration curve, NC is the number of variables in the problem, and Q is defined as in Equation 30.

IV. CALCULATIONS

The development of the equations in Chapter III, and, in particular, the reduction to practice of these equations, actually constituted the major portion of this research. For this reason, the applications of the equations for the titration of a single acid, and for a mixture of acids, will be described in some detail. The applications of the equations in the remaining sections do not differ sufficiently from the above to warrant detailed descriptions.

Utilization of the procedures developed in this work requires the availability of an electronic digital computer, preferably of large size. Much of the initial development and testing was done on an International Business Machines Type 650 computer. However, this machine is of insufficient size to contain the complete program, and final assembly and operation was done on an IBM Type 704. In general, the Fortran Automatic Coding System was used to code the programming for both machines. The program is listed in Appendix B.

A. Calculation of the Dissociation Constants for a Single Acid

A simplified flow sheet for this section is given in Figure 1. The individual steps are explained below.

1. Read in the titration curve, estimates of dissociation constants, control parameters, and any other

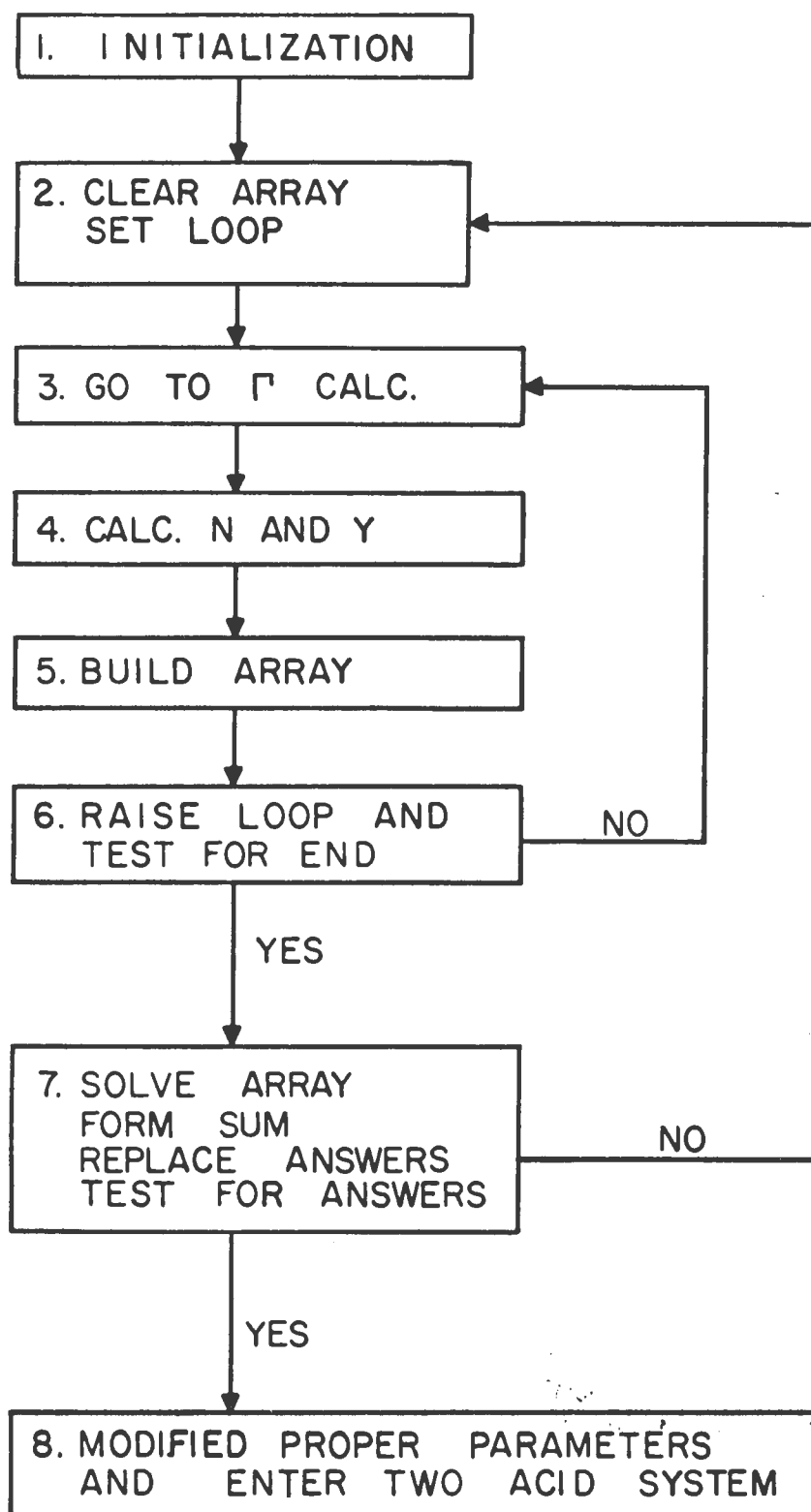


Figure 1. Flow diagram for the calculation of dissociation constants for a single acid

necessary information. The control parameters specify which of the numerous program options are to be used, and control the introduction of additional information necessary to satisfy those options. The products of the dissociation constants are formed by means of Equation 12.

2. The array specified by Equation 24 is set to zero since it is to be built up by a summation process in each iteration. The "loop" will control the successive processing of each point on the titration curve as the array is built up.
3. The "Gamma Calculator" and the operations it performs are described in detail in Section C.
4. The quantity N is calculated by means of Equation 17, and $Y = N(H^+)^n$ as shown in Equations 22 and 23.
5. The elements of the array are formed by means of Equations 22 and 23, and are added to the previous values, as indicated by Equation 24.
6. The "loop" is increased to process the next point, and a test is made to determine whether or not any points remain.
7. The array is solved by the conventional method of triangularization. The answers replace the previous values of k_i , and the sum of the absolute values of the fractional differences between the new results

and the previous results is compared with the desired closeness of fit to determine the necessity for another iteration.

8. If the last answers obtained are satisfactory, the control parameters for the two acid system (Section B) are modified to allow one pass through that section in order to calculate the standard deviations.

B. Calculation of Dissociation Constants for a Two Acid Mixture

Figure 2, detailed below, shows the basic steps employed in this treatment.

1. This step is essentially the same as Step 1 in Section A. Equation 26 is used in addition to Equation 12 to form the products of the constants.
2. The looping operation is the same as the one used in Section A. The array used in the single acid treatment does not appear in this section.
3. See Section C.
4. From Equations 16, 29, and 31, Y_C and Y_M are calculated. These quantities are vectors, there being one value of each for every point on the titration curve.
5. The partial derivatives, $\partial Y_C / \partial k$, are calculated by means of Equations 29 and 31. These will form a matrix whose dimensions are determined by the total number of dissociation constants and the number of

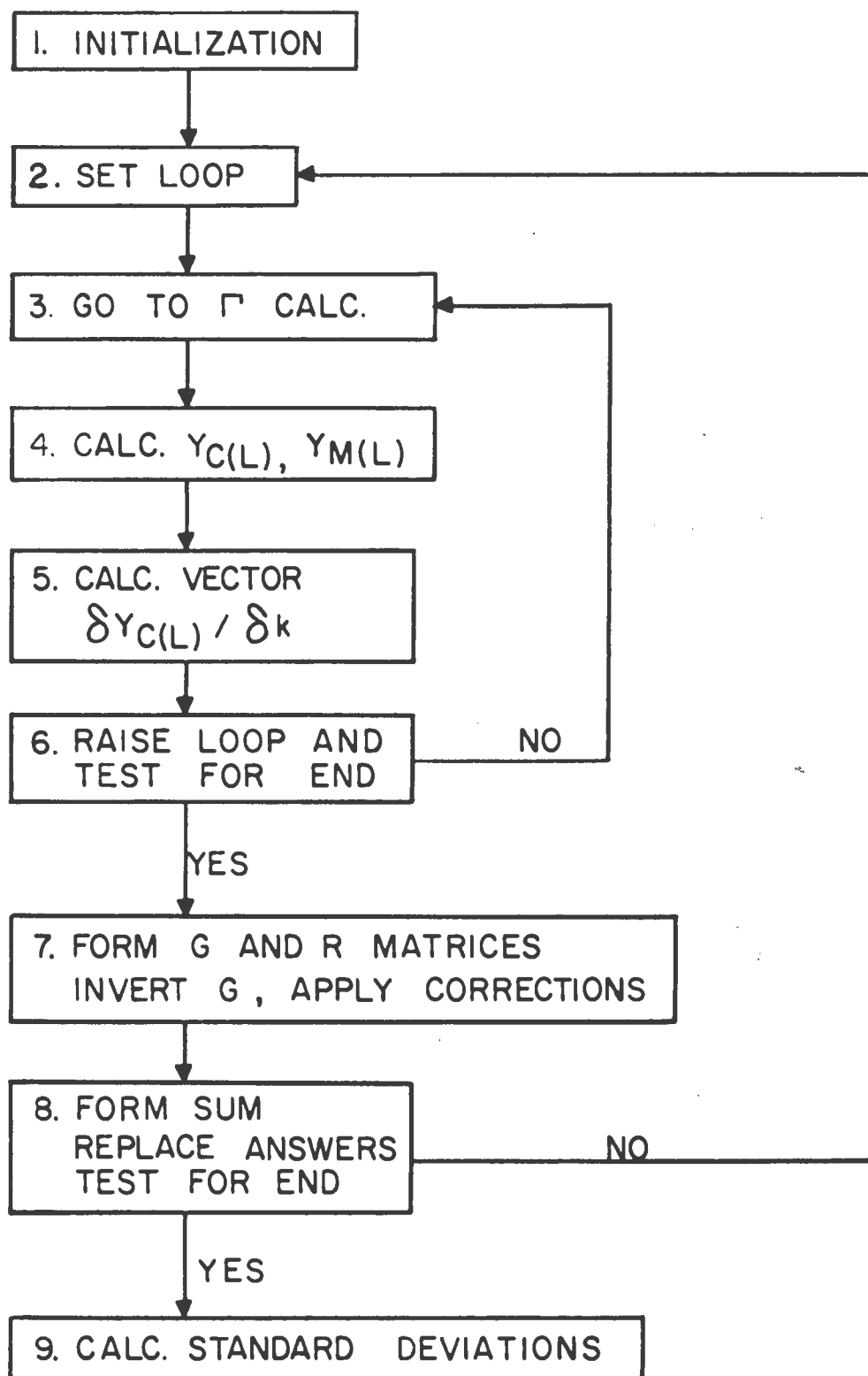


Figure 2. Flow diagram for the calculation of dissociation constants for a mixture of two acids

points on the titration curve.

6. Same as step 6 in Section A.
7. The G and R matrices, given by Equations 37 and 38, are formed and G is inverted by a standard procedure. The corrections, dk_a , are added to the dissociation constants.
8. The previous values of $k_{i,j}$ are replaced and the sum of the absolute values of the fractional changes is calculated to determine the necessity for any further iterations.
9. The standard deviations are calculated from the inverse matrix, G^{-1} , by means of Equation 41.

C. Calculation of Intermediate Quantities

This section, previously referred to as the "Gamma Calculator", computes, in addition to the activity coefficients for the various ions in solution, a large number of other necessary factors. Since the operations in this section are performed in sequence, they will be described without reference to a flow sheet.

1. The activity coefficients for the hydrogen and hydroxide ions, and for all the ionic species derived from the acids, are calculated by means of the Debye-Huckel formula, Equation 1. In the first calculation for each point, the estimated ionic strength is used.

Successive calculations use the ionic strength previously determined at the end of this section.

2. The concentrations of the acids are corrected for the volume change, caused by the addition of base, by means of the following equation.

$$C_{\text{corr}} = C_{\text{init}} \times \frac{V_{\text{init}}}{V_{\text{init}} + V_{\text{base}}} \quad 42$$

3. The sodium ion concentration is calculated from the volume of base added, its normality, and the initial solution volume.

$$[\text{Na}^+] = \frac{V_{\text{base}} \times N_{\text{base}}}{V_{\text{base}} + V_{\text{init}}} \quad 43$$

4. The concentrations of all the ionic species of the acids are calculated from the current estimates of the dissociation constants. Equation 14 is first employed to obtain the concentration of the unionized acid. Equation 11, which relates the ionic species to the unionized acid, is then utilized to obtain the individual ion concentrations.
5. The new value of ionic strength is calculated by means of Equation 2.

D. Options and Considerations

As previously mentioned, Sections C through F of Chapter III do not warrant detailed description in this work. They

do, however, add considerably to the complexity of the program because of the many branches and multiple paths of similar calculations that must be provided.

In addition to the options previously described, a number of minor options have been incorporated in the final program to increase its flexibility and utility. They include the following.

1. Hydrogen ion concentration may be in the form of pCH, paH, or pWH.
2. Ionic strength may be calculated at each point, specified for each point, or constant.
3. Hydrogen ion activity coefficients may be calculated or specified at each point.
4. Total solution volume may be calculated or constant.
5. The coefficients, A, B, and β in Equation 1 may be altered. Also, the ion size parameter for hydrogen ion, normally set at 5.0, may be changed.

The permissible decimal range of quantities in programs coded by Fortran is 10^{-38} to 10^{+38} . This range is generally sufficient, but in some problems may be greatly exceeded, causing meaningless results. Considerable attention was therefore given to providing means by which certain quantities would be automatically scaled in the proper direction when necessary, without changing the validity of any equations.

V. RESULTS

Much of the testing of the computational methods developed herein could be done only with theoretical titration curves. For the most part, these curves were calculated from various hypothetical dibasic acids. The problem of the monobasic acid is considerably less complex in many respects, and has been largely ignored since any method capable of handling dibasic acids is almost certain to be more than sufficient for monobasic acids.

Likewise, once the problem of the dibasic acid has been solved without resorting to graphical or other two dimensional limitations, additional hydrogen ions give no particular complications, in theory. In practice, the limited accuracy of experimental data will likely be the greatest problem in the treatment of polybasic acids. For these reasons, dibasic acids are the principal ones considered in this work.

A. Resolution of Successive Constants

One of the greatest problems in the calculation of acid dissociation constants has been the differentiation of successive constants whose values differ only slightly. Generally, if the ratio of the values of successive constants has been less than about 500, previous calculations have employed mathematical artifices involving questionable assumptions. It

has been calculated (14) that a break will appear in the titration curve of a dibasic acid only if the ratio of constants is over sixteen. Since there exist several acids whose reported constants differ by even lesser amounts, it is important to test the differentiating ability, or "resolving power" of any new computational method. This has been done using theoretical data, to test the ultimate limits, and with modifications to simulate experimental data in order to determine the results likely to be obtained in practice.

A series of titration curves was calculated for dibasic acids with ratios of dissociation constants varying from 1000 to 3. The initial parameters used are given in Table 1. Several of these curves have been plotted in Figure 3 to indicate the general curve shape obtained with various ratios of constants. These calculated curves are precise in pH, and within 0.001 ml of base at each point. Activity corrections were not made, since such corrections are somewhat time consuming, and ideally should have no effect on this part of the investigation. However, as a safeguard, several of the curves with low ratios of constants were also calculated with activity corrections to see if there were any effects peculiar to such corrections.

1. Ultimate resolution

These calculated curves were then processed to determine the dissociation constants, and the results are given in Table 1.

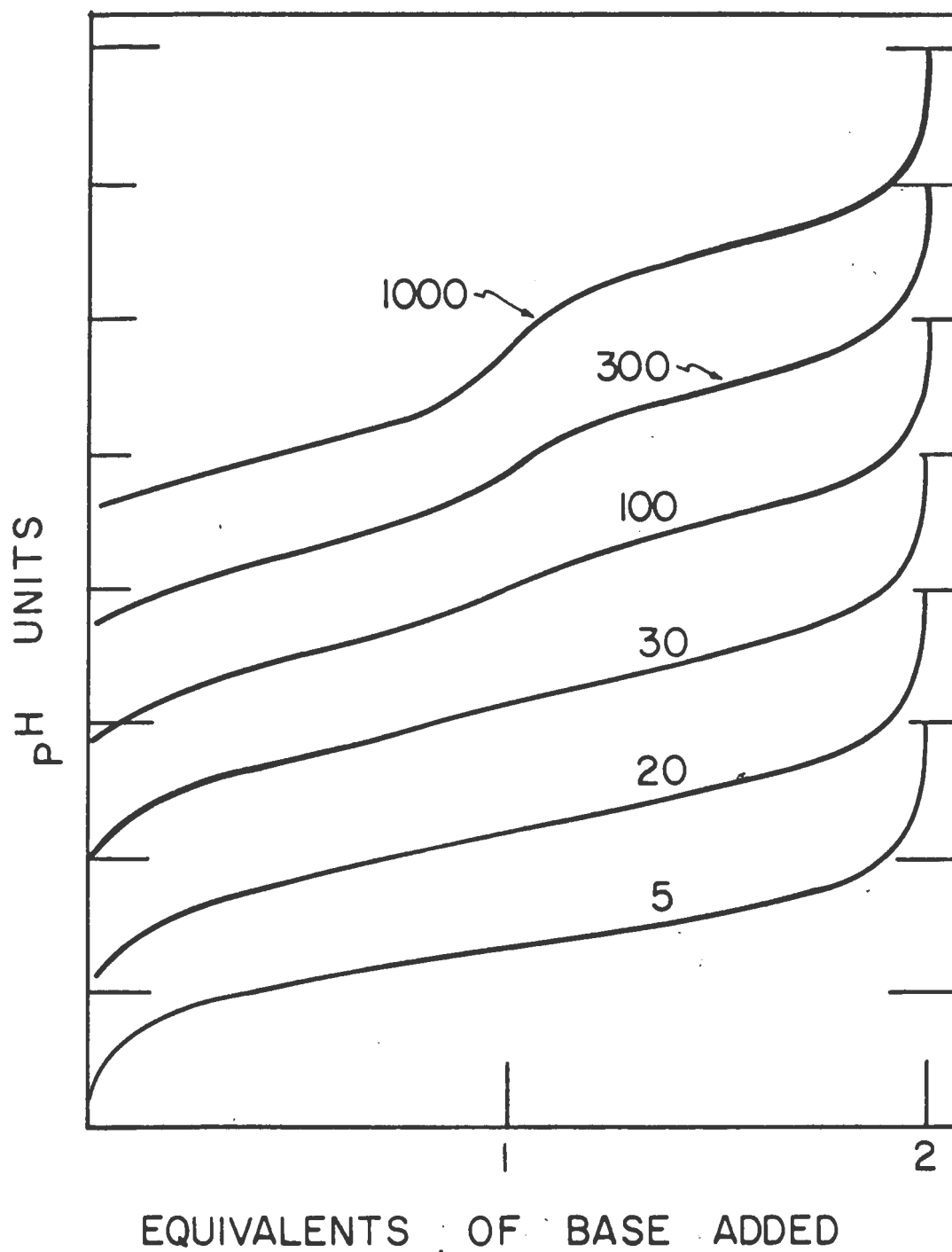


Figure 3. Calculated titration curves for various hypothetical dibasic acids with varying ratios of K_1/K_2

Table 1. Conditions and results for the theoretical test of resolving power upon titration curves of dibasic acids (Acid concentration = 0.05 M, base concentration = 0.10 N, and initial solution volume = 100.0 ml)

Initial constants		Ratio	Calculated constants		Fractional Standard deviations	
pK_1	pK_2		pK_1	pK_2	δK_1	δK_2
3.00	6.00	1000	3.00	5.99	1×10^{-5}	2×10^{-5}
3.52	6.00	300	3.52	6.00	5×10^{-6}	1×10^{-6}
4.00	6.00	100	4.00	6.00	9×10^{-6}	3×10^{-7}
4.52	6.00	30	4.52	6.01	2×10^{-5}	1×10^{-7}
4.60	6.00	25	4.60	6.00	1×10^{-5}	7×10^{-8}
4.70	6.00	20	4.70	6.00	4×10^{-5}	1×10^{-6}
4.82	6.00	15	4.82	6.00	2×10^{-5}	4×10^{-8}
5.00	6.00	10	5.00	6.01	7×10^{-5}	9×10^{-8}
5.30	6.00	5	5.30	5.99	1×10^{-4}	4×10^{-8}
5.52	6.00	3	5.52	6.00	1×10^{-4}	2×10^{-8}
5.00 ^a	6.00	10	5.00	6.00	6×10^{-6}	6×10^{-9}
5.52 ^a	6.00	3	5.52	6.00	5×10^{-4}	8×10^{-8}

^aWith activity corrections

It is evident from these results that this method is inherently capable of excellent resolution. It is instructive to note, however, that the answers obtained are not always exactly equal to the constants used to calculate the titration curves. An error of 0.01 in pK is equivalent to an error of about 2% in K , and in several cases such errors were obtained. These errors are not reflected in the standard deviations, since this latter quantity is merely a measure of how well the answers fit the data, and not a measure of how accurate the answers are.

The inclusion of corrections for activity caused no difficulties.

2. Effects of errors

A consistent error in experimental data may result in a titration curve that is smooth and satisfactory in appearance when plotted, but is nevertheless inaccurate. An error of up to 0.05 units in the standardization of a pH meter might not be unexpected under certain circumstances. To determine the effects of such an error, the pH values of the calculated curves were all changed by the same amount, and the resulting data processed to obtain the constants. The results are given in Table 2.

The changes in pK_1 are quite consistent and not alarmingly large. The changes in pK_2 are considerable, and no posi-

Table 2. Conditions and results for the test of the effect upon dissociation constants of a consistent error in the titration curve

Initial constants		Calculated constants with +0.05 pH unit error		Calculated constants with -0.05 pH unit error	
pK ₁	pK ₂	pK ₁	pK ₂	pK ₁	pK ₂
3.00	6.00	3.09	4.61	2.91	Neg.
3.52	6.00	3.61	4.80	3.43	"
4.00	6.00	4.08	5.04	3.91	"
4.52	6.00	4.61	5.25	4.44	"
4.60	6.00	4.69	5.18	4.51	"
4.70	6.00	4.77	5.65	4.63	"
4.82	6.00	4.90	5.58	-- a	-a
5.00	6.00	5.08	5.47	4.92	Neg.
5.30	6.00	5.37	5.74	5.23	"
5.52	6.00	5.60	5.63	5.44	"
5.00 ^b	6.00	5.08	5.64	4.92	"
5.52 ^b	6.00	5.60	5.76	5.44	"

^aThis calculation was not completed

^bWith activity corrections

tive values were obtained when the pH values were lowered.

Activity corrections gave no change in pK_1 , but did affect pK_2 . The reason for this is not known.

Experimental titration curves are unlikely to exhibit the precision demanded of the calculated curves, nor, it is hoped, will they have a consistent error of disturbing magnitude. What will be found are random errors of multiple origin. A precise determination of the effects of such errors is more than likely impossible. Since acids with suitably spaced constants are not readily available (if at all), and experimental titrations are not sufficiently accurate, attempts to determine the effects of random errors must be made with calculated data suitably modified to include such errors. Ideally, the errors should be applied to both pH and titrant volume readings, but this would seem to be an unnecessary complication for what can at best be only an approximation. Thus, only the pH data were modified. McComas and Rieman (19) estimated the accuracy of pH measurements with a glass electrode as ± 0.03 units. Although other electrodes may be subject to less error, it was considered reasonable to subject the pH data to a standard deviation of 0.05 units. A table of random digits, in conjunction with the standard Gaussian Distribution Curve, was used to calculate the error to be applied. Table 3 gives the direction and magnitude of the error assigned for each digit.

Table 3. Errors in pH assigned by random digit table for
Sigma = 0.05

Digits		Error
+	-	
0	5	0.006
1	6	0.020
2	7	0.034
3	8	0.072
4	9	0.083

All calculated curves were treated identically, and for a 28 point curve, the average deviation applied was -0.01 units. The results of the dissociation constant determinations from these modified curves are given in Table 4.

Table 4. Conditions and results for the test of the effect upon dissociation constants of random errors in the titration curve

Initial constants		Calculated constants	
pK ₁	pK ₂	pK ₁	pK ₂
3.00	6.00	2.84	Neg.
3.52	6.00	3.54	6.33
4.00	6.00	4.10	4.30
4.52	6.00	4.49	5.45
4.60	6.00	4.57	5.49
4.70	6.00	4.60	Neg.
4.82	6.00	4.72	Neg.
5.00	6.00	4.88	Neg.
5.30	6.00	5.29	5.85
5.52	6.00	5.51	5.82
5.00 ^a	6.00	4.89	Neg.
5.52 ^a	6.00	5.51	5.92

^aWith activity corrections

Once again, it is pK_2 that is predominantly affected, both with and without activity corrections. However, the errors are consistent neither in direction nor magnitude.

B. Resolution of Mixtures

The mathematical resolution of a mixture of acids is considerably more difficult than the resolution of successive constants of a single acid. The first test was made upon a calculated curve for a monobasic acid, $pK = 5$, treating this curve as a mixture of monobasic acids in varying concentration ratios, with the total concentration equal to that used in calculating the curve. Ideally, the computations should result in values of 1.0×10^{-5} for both constants. The results given in Table 5 indicate that this ideal was approached rather closely.

Table 5. Conditions and results for the mathematical treatment of a single monobasic acid as a mixture of two monobasic acids

Molar concentrations		Dissociation constants $\times 10^5$	
Acid 1	Acid 2	Acid 1	Acid 2
0.0500	0.0000	1.000	----
0.0495	0.0005	1.000	1.02
0.0490	0.0010	.999	1.05 ^a
0.0475	0.0025	.999	1.02 ^a
0.0450	0.0050	1.00	.995
0.0425	0.0075	.998	1.01
0.0400	0.0100	.999	1.00
0.0350	0.0150	1.00	.995
0.0300	0.0200	.991	1.01
0.0250	0.0250	1.00	.997

^aBetter values were obtained in these runs

As mentioned in Chapter IV, this part of the program is reiterative. Such methods may occasionally oscillate around the correct answer, or perhaps even diverge, rather than converge to a final solution. In the runs in Table 5, oscillation was encountered. Ten iterations were permitted in each run, and the answers were taken from the iteration which gave the smallest least-squares parameter. This was usually the best answer, although there were exceptions in two cases.

A calculated curve for what might be considered a typical acid mixture was then processed; the results are given in Table 6. No difficulties were encountered in this calculation.

Table 6. Conditions and results for the resolution of a mixture of a monobasic and a dibasic acid (Concentration of each acid = 0.01 M)

		Dissociation constants	
		given	found
Acid 1	K_1	6.40×10^{-5}	6.41×10^{-5}
	K_2	2.70×10^{-6}	2.69×10^{-6}
Acid 2		1.77×10^{-4}	1.77×10^{-4}

C. Consistency

Experimental consistency was examined by titrating aliquots of a tartaric acid solution with sodium hydroxide, using a glass electrode. The pH meter was standardized against 0.05 M potassium biphthalate at the beginning of each titration.

There was no significant drift. The constants obtained from these titrations, with activity corrections applied, are given in Table 7.

Table 7. Conditions and results for repetitive titrations of tartaric acid (Initial volume = 100.0 ml, acid concentration = 0.1031 M, base concentration = 0.05 N)

Dissociation constants		Standard deviations	
$K_1 \times 10^4$	$K_2 \times 10^5$	$K_1 \times 10^6$	$K_2 \times 10^{10}$
8.64	4.34	6.24	12.5
8.64	4.35	5.34	10.7
8.81	4.28	4.33	8.8
9.33	4.19	3.76	7.8
8.34	4.31	5.32	10.5
10.07	4.12	2.41	5.2
10.05	4.17	3.00	6.5

Although 12 to 14 pH measurements were made in each titration, and all reasonable care was taken, there are considerable variations in the results. Here, unlike the tests with calculated data, it is K_1 that shows the greatest variation, with values that bracket the commonly accepted 9.6×10^{-4} . The variations in K_2 are much smaller than those in K_1 , but the values differ somewhat from the accepted one of 2.9×10^{-5} . Once again, the standard deviation is obviously not a valid indication of the accuracy of the computed constants.

D. Improper Calculations

The errors introduced by treating a dibasic acid as a mixture of monobasic acids were investigated by processing the

single acid calculated data as mixtures. From the results given in Table 8, it can be seen that this procedure will produce very good results when the ratio of constants is 100 or more, and reasonably good results are obtained at even lower ratios. Below a ratio of 10, results were unsatisfactory.

Table 8. Conditions and results for the test of the effect upon dissociation constants of the treatment of a dibasic acid as a mixture of two monobasic acids

Initial constants		Calculated constants	
pK_1	pK_2	pK_1	pK_2
3.00	6.00	3.00	5.99
3.52	6.00	3.52	6.00
4.00	6.00	4.00	5.99
4.52	6.00	4.54	5.99
4.60	6.00	4.62	5.99
4.70	6.00	4.72	5.97
4.81	6.00	4.86	5.97
5.00	6.00	5.05	5.96
5.30	6.00	Neg.	3.72
5.52	6.00	5.39	Neg.

E. Experimental Titrations

In addition to the titrations of tartaric acid previously mentioned, titrations were made on acetic acid, succinic acid, and on mixtures of tartaric and acetic, succinic and acetic, and tartaric and succinic acids. The last three would provide a severe experimental test of the resolving power of the method for mixtures. Unfortunately, of these three, only the last produced any positive results. From Table 9, it can be seen that the single acids approached the literature values fairly

closely, and the values for tartaric acid in the mixture are very close to the commonly accepted values. However, negative constants were obtained for succinic acid in this mixture.

Table 9. Results of experimental titrations of various single acids and mixtures

Acid	Constant	Experimental value	Literature value
Acetic	K	1.66×10^{-5}	1.75×10^{-5}
Succinic	K ₁	5.96×10^{-5}	6.6×10^{-5}
	K ₂	2.18×10^{-6}	2.8×10^{-6}
Tartaric + Succinic	Tar. K ₁	9.81×10^{-4}	9.6×10^{-4}
	Tar. K ₂	2.88×10^{-5}	2.9×10^{-5}
	Suc. K ₁	Neg.	
	Suc. K ₂	Neg.	

Data for the titrations giving successful results are tabulated in Appendix A.

VI. DISCUSSION

The computational procedures developed in this work have been shown; it is believed, to be fundamentally sound and inherently extremely accurate. However, the accuracy that can be attained in practice, by any method, may be far poorer than generally expected.

Successive dissociation constants of small ratio, a major obstacle in most former methods, have been shown to present no difficulties attributable to such ratios. The thoroughly satisfactory manner in which closely spaced constants are resolved is not, however, accompanied by equally satisfactory accuracy. It is this latter fact which casts some suspicion upon all constants previously determined by titration methods. It should be emphasized that the matter of accuracy is largely an experimental problem, and neither necessarily nor probably a fundamental limitation of the method. Since the "titrations" used for testing were calculated by reiterative methods, some tolerance had to be allowed. This was in the volume of base, which was within 0.001 ml at every point in a titration requiring 100.0 ml. Such accuracy in practice would be attainable only with exceptional care, even in weight titrations. Although, as shown, this may lead to a 2% error in dissociation constants, it is not unusual to find literature values expressed to three significant figures when even the

second is probably uncertain. Other experimental methods may involve less error, but they can not be judged in this work.

Consistent pH errors produce effects somewhat greater than anticipated. For a monobasic acid, it might be expected that the change in pK would essentially equal the change in pH. Such a test was not made, but it now appears that the effect might not be quite so simple. The dibasic acid tests demonstrate that a simple displacement of the titration curve gives a not so simple displacements of pK s. An analysis of the mathematical niceties involved in these displacements would have little practical value. However, two simple and constructive conclusions can be drawn. First, the magnitude of errors to be expected, if the work is performed with care, has been overestimated. Second, the effect of such errors as may be present can be considerable. These conclusions are also consistent with the experimental titrations done in this work.

When considering the results of introducing random errors into the titration curves, it is well to remember that the curves do not retain their original shape, nor are they altered identically in two dimensions. With this in mind, one may conclude that the rather random results indicate excessive pessimism in the estimation of likely experimental error; this is then essentially the same result as obtained for consistent errors.

Mixtures of acids proved to be no more difficult to re-

solve than single acids, within limits. Certainly the results given in Tables 5 and 6 are as good as one could reasonably expect. However, more severe examples, such as mixtures of dibasic acids with overlapping constants, proved to be insoluble. Inaccuracies in the data are the most reasonable explanation for this failure. It is possible that titration data accurate to more significant figures would enable satisfactory resolution to be attained, but there would be no practical application. The almost total failure of the experimental titrations of mixtures to be properly resolved is not surprising. The solitary exception cannot be explained. In general, titration of acid mixtures does not appear to be a fruitful undertaking, unless there is considerable separation of constants.

The multiple titrations of tartaric acid give an indication of the results likely to be obtained by ordinary analytical procedures. These titrations were not the ultimate in refinement nor accuracy, but were typical of ordinary laboratory practice. Better results would be desired, but the range of pK_1 , 3.00 - 3.08, is not unreasonable in view of the previous tests, and pK_2 , 4.36 - 4.39, covers an almost remarkably small range.

The "accepted" values, to which these results were compared in section V, are not to be considered as ultimate standards for comparison. They are perhaps the most widely accepted, but a cursory search of published constants will re-

veal both higher and lower values than those obtained in this work. For this reason, consistency is considered to be a more important criterion than conformance to any other particular work. On that basis, and in view of the effects of errors, these titrations may be considered quite satisfactory.

The errors that resulted by assuming a dibasic acid to be a mixture of monobasic acids were not as extensive as anticipated. If all other factors are equal, the ratio of constants may apparently be as small as 100 without introducing appreciable errors. There is no merit in such an assumption if computing methods and facilities of the type used in this work are available, (in fact the mixture involves more work), but it does indicate that the limits of 500 to 1000 used by others are rather conservative. And that is, perhaps, the only assumption in previous calculations that is conservative.

VII. SUMMARY

The primary goal of this work has been attained; dissociation constants have been calculated without use of simplifying assumptions, and with full consideration of all available data. Errors in the data have a considerable effect on the answers obtained, and some calculations are simply not possible due to experimental inaccuracies.

Many literature values must now be accepted with reservation for several reasons. These include unjustified or unnecessary simplifications in calculations, and the use of different pH scales in older work.

Extremely accurate titrations are required to obtain dissociation constants of two or more significant figures, particularly for polybasic acids. If good data are available, however, the mathematical means to make full use of them are now at hand.

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X. APPENDIX A

Table 10. Data for titrations of tartaric acid
 Acid concentration = 0.01031 M; base concentration = 0.0501 N; initial solution volume = 50.00 ml.

Ml of base	Solution pH						
	1	2	3	4	5	6	7
4.00	2.98	2.98	2.97	2.96	2.99	2.94	2.94
8.50	3.45	3.45	3.45	3.44	3.46	3.43	3.43
12.50	3.94	3.94	3.93	3.93	3.94	3.91	3.90
16.50	4.47	4.46	4.47	4.47	4.49	4.45	4.45
19.00	5.04	5.02	5.05	5.03	5.05	5.01	5.01
20.00	5.66	5.67	5.70	5.67	5.70	5.67	5.68
20.20	5.99	5.98	6.07	6.00	6.06	5.99	6.00
20.30		6.34	6.43	6.30	6.48	6.32	6.38
20.40	6.95	7.00	7.11	7.01	7.20	7.01	7.00
20.45		7.55	7.58	7.50	7.87	7.70	7.55
20.50	8.17	8.39		8.30	8.55	8.40	8.30
20.52			8.56				

Table 11. Data for titration of acetic acid
 Acid concentration = 0.02174 M; base concentration = 0.0501 N; initial solution volume = 50.00 ml.

Ml of base	Solution pH
1.00	3.56
3.00	3.99
6.00	4.32
10.00	4.67
14.00	5.00
18.00	5.45
20.00	5.85
21.00	6.34
21.30	6.70
21.50	7.26

Table 12. Data for titration of succinic acid
 Acid concentration = 0.01051 M; base concentration = 0.0501 N; initial solution volume = 50.00 ml.

Ml of base	Solution pH
2.00	3.63
4.50	4.05
7.50	4.46
10.50	4.87
13.50	5.28
16.50	5.70
18.50	6.08
19.60	6.41
20.20	6.73
20.60	7.17

Table 13. Data for titration of tartaric and succinic acid mixture (Acid concentrations = 0.01031 M and 0.010437 M; base concentration = 0.0501 N; initial solution volume = 100.00 ml.)

Ml of base	Solution pH	Ml of base	Solution pH
1.00	2.77	26.00	4.63
2.00	2.84	27.00	4.70
3.00	2.92	28.00	4.80
4.00	3.00	29.00	4.89
5.00	3.09	30.00	4.99
6.00	3.15	31.00	5.09
7.00	3.23	32.00	5.20
8.00	3.31	33.00	5.30
9.00	3.40	34.00	5.40
10.00	3.48	35.00	5.53
11.00	3.55	36.00	5.65
12.00	3.62	37.00	5.80
13.00	3.70	38.00	5.95
14.00	3.77	39.00	6.18
15.00	3.86	39.50	6.31
16.00	3.92	40.00	6.50
17.00	4.00	40.20	6.60
18.00	4.05	40.40	6.71
19.00	4.12	40.60	6.84
20.00	4.19	40.80	7.05
21.00	4.26	41.00	7.35
22.00	4.32	41.10	7.55
23.00	4.40		
24.00	4.48		
25.00	4.55		

XI. APPENDIX B

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C
C
C
C
C      WAYNE DUNNING, IOWA STATE UNIVERSITY
C      THIS PROGRAM CALCULATES DISSOCIATION CONSTANTS AND THEIR STANDARD
C      DEVIATIONS FOR A SINGLE ACID OR A MIXTURE OF TWO ACIDS.  PRINCIPAL
C      INPUT DATA CONSIST OF A PH TITRATION CURVE AND KNOWN ACID CONCEN-
C      TRATIONS.  IN ADDITION, CONCENTRATIONS MAY BE CALCULATED FROM A
C      TITRATION CURVE AND KNOWN CONSTANTS, OR A THEORETICAL TITRATION
C      CURVE MAY BE COMPUTED.  OPTIONS INCLUDE THE TITRATION OF A BASE,
C      OR OF A SALT OF A WEAK ACID OR BASE.
C
C      DIMENSION  JUNK1(40), JUNK2(40,2), JUNK3(40)
00000 DIMENSION SIZION(6), CKPROD(6), CKIND(6), HAION(8), HYDACT(4),      WWD1100
000001 OHACT(4), CMU(51), PH(51), ACTCFH(51), GAMMA(6), TNTML(51),      WWD1026
000002 FACTOR(6), ACTSCL(7), RESULT(6), AR(50,6), E(14), FC(50), FM(50), WWD1002
000003 DF(50), G(40,40), R(40,1), U(6,6)                                WWD
000004 SUM, Q, Q1, NDPTS, CMLTNT, RQDCL, VOLTL, CNA, VOLC, CLION
C      COMMON  JUNK1, JUNK2, JUNK3
00000 COMMON SIZION, CKPROD, CKIND, HAION, HYDACT, OHACT, CMU, PH,      WWD1007
000001 ACTCFH, GAMMA, TNTML, FACTOR, ACTSCL, RESULT, AR, E, FC, FM, DF, WWD1008
000002 G, R, U, ACID1, ACID2, CACID1, CACID2, NACIDS, NCON1, NCON2,      WWD1009
000003 NCONT, DENOM1, DENOM2, VNUM1, VNUM2, SCFTR, FN, Y, FB, MSCALE, WWD1010
000004 SUM, Q, Q1, NDPTS, CMLTNT, RQDCL, VOLTL, CNA, VOLC, CLION      WWD1011
C      BEGINNING OF PROGRAM.  THIS SECTION IS PRIMARILY FOR PROPER
C      INITIALIZATION OF THE PROGRAM.  THE NECESSARY DATA IS READ IN, AND
C      THE VALUES OF CERTAIN CONSTANTS ARE SET.
C      SET ICN SIZE PARAMETERS, DISSOCIATION CONSTANTS, AND INDIVIDUAL
C      ION CONCENTRATIONS TO ZERO
00401 DO 403 I = 1, 6
00000 SIZION(I) = 0.
00000 RESULT(I) = 0.
00000 CKPROD(I) = 0.
00403 CKIND(I) = 0.
00000 DO 405 I = 1, 8
00405 HAION(I) = 0.
C
C      ZERO POWER OF HYDROGEN AND HYDROXIDE ACTIVITY EQUALS ONE
00000 HYDACT(1) = 1.
00000 OHACT(1) = 1.
C
C      UNLESS OTHERWISE SPECIFIED, HYDROGEN ION SIZE IS 5
C      HIONSZ = 5.
C
C      UNLESS OTHERWISE SPECIFIED, TEMPERATURE IS 25 DEGREES, AND DEBYE
C      HUCKEL COEFFICIENTS ARE
00000 DBHFA = 0.5092
00000 DBHFB = 0.3286
C
C      UNLESS OTHERWISE SPECIFIED, BETA IN D-H FORMULA IS ZERO
C      BETADH = 0.
C
C      WRITE HEADING, READ AND WRITE OPENING STATEMENT
00000 WRITE OUTPUT TAPE 9, 8
00000 READ 10
00000 WRITE OUTPUT TAPE 9, 10
00000 PUNCH 10
C
C      READ CONTROL PARAMETERS
00000 READ 12, NTYPE1, NTYPE2, NTYPE3, NTYPE4, NTYPE5, NTYPE6, NTYPE7,
000001 NTYPE8, NTYPE9
C
C      WRITE TYPE OF CALCULATION TO BE DONE IN THIS PARTICULAR RUN

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00407 GO TO (413, 411, 409), NTYPE1                                WWD1129
00409 WRITE OUTPUT TAPE 9, 14                                       WWD1130
00000 GO TO 415                                                       WWD1131
00411 WRITE OUTPUT TAPE 9, 16                                         WWD1132
00000 GO TO 415                                                       WWD1133
00413 WRITE OUTPUT TAPE 9, 18                                         WWD1134
C                                                                      WWD1135
C
C      READ ACID CONCENTRATIONS, AND WRITE WITH APPROPRIATE COMMENT
C      DEPENDING UPON WHETHER CONCENTRATION IS EXACT, OR AN INITIAL
C      ESTIMATE. IF THERE IS ONLY ONE ACID, THE CONCENTRATION OF THE
C      SECOND IS ZERO.
00415 READ 20, ACID1, ACID2                                           WWD1137
00417 GO TO (421, 421, 419), NTYPE1                                   WWD1138
00419 WRITE OUTPUT TAPE 9, 22, ACID1, ACID2                           WWD1139
00000 GO TO 423                                                       WWD1140
00421 WRITE OUTPUT TAPE 9, 24, ACID1, ACID2                           WWD1141
C                                                                      WWD1142
C
C      READ INITIAL VOLUME OF SOLUTION IN ML., NORMALITY OF TITRANT,
C      IONIC STRENGTH (AN ESTIMATE UNLESS VALUE IS CONSTANT), MOLAR CON-
C      CENTRATION OF ANY ADDED MONOVALENT SALT, DISSOCIATION CONSTANT OF
C      WATER, AND DESIRED CLOSENESS OF FIT OF RESULTS IN PERCENT
00423 READ 26, SOLNV, BASEN, GMU, CKNO3, WCON, ERROR                 WWD1147
C
C      WRITE THE ABOVE QUANTITIES
00000 WRITE OUTPUT TAPE 9, 28, SOLNV, BASEN, GMU, CKNO3, WCON, ERROR WWD1149
C                                                                      WWD1150
C      READ THE INDIVIDUAL DISSOCIATION CONSTANTS OR THE ESTIMATED VALUES
C      OF THEM. THE FIRST FOUR ARE FOR THE FIRST ACID, THE LAST TWO FOR
C      THE SECOND ACID. ANY CONSTANT WHICH DOES NOT EXIST MUST HAVE A
C      VALUE OF ZERO.
00000 READ 30, (CKIND(I), I = 1, 6)                                   WWD1152
C
C      WRITE INDIVIDUAL DISSOCIATION CONSTANTS WITH COMMENTS
00425 GO TO (429, 427, 427), NTYPE1                                   WWD1154
00427 WRITE OUTPUT TAPE 9, 32, (CKIND(I), I = 1, 6)                 WWD1155
00000 GO TO 431                                                       WWD1156
00429 WRITE OUTPUT TAPE 9, 34, (CKIND(I), I = 1, 6)                 WWD1157
C
C      IF ACTIVITY CORRECTIONS ARE NOT TO BE MADE, WRITE THIS FACT, SET
C      ALL VALUES OF IONIC STRENGTH TO ZERO, AND DO NOT READ IN THE ION
C      SIZE PARAMETERS.
00431 GO TO (435, 433, 435), NTYPE2                                   WWD1158
00433 WRITE OUTPUT TAPE 9, 36                                         WWD1161
00000 DO 434 I = 1, 50                                               WWD1162
00434 CMU(I) = 0.                                                    WWD1163
00000 GO TO 437                                                       WWD1164
C
C      READ AND WRITE THE ION SIZE PARAMETERS. VALUES FOR NONEXISTENT
C      IONS SHOULD BE ZERO.
00435 READ 38, (SIZION(I), I = 1, 6)                                   WWD1166
00000 WRITE OUTPUT TAPE 9, 40, (SIZION(I), I = 1, 6)                 WWD1167
C
C      IF IONIC STRENGTH IS SPECIFIED AS CONSTANT, WRITE ITS VALUE AND
C      SET ALL STORAGE VALUES TO IT.
00437 GO TO (440, 439, 443), NTYPE3                                   WWD1168
00439 WRITE OUTPUT TAPE 9, 42, GMU                                     WWD1172
00440 DO 441 I = 1, 50                                               WWD1173
00441 CMU(I) = GMU                                                    WWD1174
C
C      IF VOLUME IS SPECIFIED AS CONSTANT, WRITE THIS FACT AND THE VALUE

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00443 GO TO (447, 445), NTYPE4                                WWD1175
00445 WRITE OUTPUT TAPE 9, 44, SOLNV                          WWD1177
C
C   WRITE THE TYPE OF PH READING SPECIFIED BY CONTROL PARAMETER 5
00447 GO TO (453, 451, 449), NTYPE5                          WWD1178
C   WRITE THAT PWH IS USED
00449 WRITE OUTPUT TAPE 9, 46                                WWD1180
00000 GO TO 455                                              WWD1181
C   WRITE THAT PCH IS USED
00451 WRITE OUTPUT TAPE 9, 48                                WWD1183
00000 GO TO 455                                              WWD1184
C   WRITE THAT PAH IS USED
00453 WRITE OUTPUT TAPE 9, 50                                WWD1186
C
C   READ AND WRITE ION SIZE PARAMETER FOR HYDROGEN IF VALUE IS NOT 5.0
00455 GO TO (459, 457), NTYPE6                                WWD1187
00457 READ 52, HIONSZ                                         WWD1190
00000 WRITE OUTPUT TAPE 9, 54, HIONSZ                         WWD1191
C
C   READ AND WRITE NEW D-H COEFFICIENTS A AND B IF TEMPERATURE IS NOT
C   25 DEGREES
00459 GO TO (463, 461), NTYPE7                                WWD1192
00461 READ 56, DBHFA, DBHFB                                   WWD1194
00000 WRITE OUTPUT TAPE 9, 58, DBHFA, DBHFB                  WWD1195
C
C   READ AND WRITE BETA IN D-H FORMULA IF BETA IS TO BE USED
00463 GO TO (467, 465), NTYPE8                                WWD1196
00465 READ 60, BETADH                                         WWD1198
00000 WRITE OUTPUT TAPE 9, 62, BETADH                         WWD1199
C
C   WRITE THE TYPE OF TITRATION SPECIFIED BY CONTROL PARAMETER 9
00467 GO TO (475, 473, 471, 469), NTYPE9                     WWD1200
C   WRITE SALT OF BASE TITRATED WITH BASE
00469 WRITE OUTPUT TAPE 9, 64                                WWD1203
00000 GO TO 477                                              WWD1204
C   WRITE BASE TITRATED WITH ACID
00471 WRITE OUTPUT TAPE 9, 66                                WWD1206
00000 GO TO 477                                              WWD1207
C   WRITE SALT OF ACID TITRATED WITH ACID
00473 WRITE OUTPUT TAPE 9, 68                                WWD1209
00000 GO TO 477                                              WWD1210
C   WRITE ACID TITRATED WITH BASE
00475 WRITE OUTPUT TAPE 9, 70                                WWD1212
C   COUNT NUMBER OF ACIDS
00477 NACIDS = 1                                             WWD1213
00479 IF (ACID2) 901, 483, 481                               WWD1214
00481 NACIDS = 2                                             WWD1215
C   COUNT NUMBER OF DISSOCIATION CONSTANTS FOR FIRST ACID
00483 NCON1 = 0                                              WWD1216
00000 DO 489 I = 1, 4                                         WWD1217
00485 IF (CKIND(I)) 902, 489, 487                             WWD1218
00487 NCON1 = NCON1 + 1                                       WWD1219
00489 CONTINUE                                              WWD1220
00911 NCON2 = 0                                              WWD1221
C   COUNT DISSOCIATION CONSTANTS FOR SECOND ACID, IF ANY
04913 GO TO (4923, 4915), NACIDS                              WWD1222
C   AN INITIALIZATION FOR NON-LINEAR LEAST SQUARES, IF THERE ARE
C   TWO ACIDS
04915 QOD = 1000.                                           WWD1223

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C      MAXIMUM NUMBER OF ITERATIONS ALLOWED PER PASS IN N-L LEAST SQS.
00000 NID = 5
00000 DO 4921 I = 5, 6
04917 IF (CKIND(I)) 913, 4921, 4919
04919 NCON2 = NCON2 + 1
04921 CONTINUE
C
C      TOTAL NUMBER OF CONSTANTS
04923 NCONT = NCON1 + NCON2
C
C      ABSOLUTE ERROR
00000 ERROR = ERROR / 100.
C
C      OBTAIN PRODUCTS OF DISSOCIATION CONSTANTS
C      RESET OVERFLOW TRIGGER
00000 IF ACCUMULATOR OVERFLOW 4925, 4925
04925 CKPROD(1) = CKIND(1)
00000 DO 4927 I = 2, NCON1
04927 CKPROD(I) = CKPROD(I - 1) * CKIND(I)
04929 GO TO (4933, 4931), NACIDS
04931 CKPROD(5) = CKIND(5)
00000 CKPROD(6) = CKIND(5) * CKIND(6)
C      ERROR STOP IF A PRODUCT OF CONSTANTS IS OUT OF RANGE
00000 IF ACCUMULATOR OVERFLOW 909, 4933
C      TRANSFER TO PROPER SECTION OF PROGRAM DEPENDING ON TYPE OF
C      CALCULATION BEING DONE
04933 GO TO (101, 201, 301), NTYPE1
C
C      SUBMASTER PROGRAM TO DETERMINE DISSOCIATION CONSTANTS
C
C      GO TO READ IN TITRATION CURVE
00101 GO TO 501
C
C      RETURN FROM CURVE READ IN. DETERMINE MATRIX SIZE FOR SINGLE ACID
00103 NROWS = NCON1
00000 NCOLMS = NROWS + 1
C
C      SET ITERATION COUNTER AND SCALE CHANGE CHECKER TO ZERO
C      CHECKER PREVENTS AN ATTEMPT TO SCALE IN BOTH DIRECTIONS
C      SCALING IS NECESSARY TO KEEP DECIMAL POINT WITHIN ALLOWABLE RANGE
00000 MSCL = 0
00000 MCOUNT = 0
C      MCLLD = 0
C      INITIAL SCALING FACTOR EQUALS ZERO
00000 SCFTR = 0.
C      SET NONLINEAR ERROR FACTOR
00000 ERQD = .0001 * FLOATF(NDPTS)
C
C      GET SCALING QUANTITY
00000 IF ACCUMULATOR OVERFLOW 105, 105
00105 ACTSCL(1) = 10. ** (SCFTR * FLOATF(NCONT))
C      ERROR STOP IF SCALING QUANTITY OUT OF RANGE
00000 IF ACCUMULATOR OVERFLOW 906, 107
C
C      SET NONLINEAR ITERATION COUNTER TO ZERO
00107 LLD = 0
C      CLEAR RESULTS AND ARRAY FOR SINGLE ACID
00109 GO TO (111, 115), NACIDS
00111 DO 113 I = 1, NROWS
00000 RESULT(I) = 0.
00000 DO 113 J = 1, NCOLMS
00113 AR(I, J) = 0.

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C
C   INITIALIZE LOOP AND GO TO ACTIVITY CORRECTION SECTION (GAMMA
C   CALCULATOR)
00115 K = 1                                WWD1427
C   OPTIONAL OUTPUT
C       IF (SENSE SWITCH 1) 116, 801
116 WRITE OUTPUT TAPE 9, 61
00000 GO TO 801                            WWD1428
C                                           WWD1429
C   RETURN FROM GAMMA CALCULATOR AND BRANCH ON TITRATION TYPE
00117 GO TO (125, 125, 119, 119), NTYPE9   WWD1430
C                                           WWD1431
C   OBTAIN SCALED HYDROXIDE ACTIVITIES
00119 DO 123 I = 1, NCONT                  WWD1432
00123 ACTSCL(I + 1) = ACTSCL(I) * OHACT(2) WWD1433
C   TOTAL NEGATIVE ION CONCENTRATION
00000 FN = -HYDACT(2) / GHYDRO - CNA + COH + CLION WWD1434
00000 GO TO 131                            WWD1435
C                                           WWD1436
C   OBTAIN SCALED HYDROGEN ACTIVITIES
00125 DO 129 I = 1, NCONT                  WWD1437
00129 ACTSCL(I + 1) = ACTSCL(I) * HYDACT(2) WWD1438
C   TOTAL POSITIVE ION CONCENTRATION
00000 FN = HYDACT(2) / GHYDRO + CNA - COH - CLION WWD1439
C                                           WWD1440
C   SCALED FN TIMES PROPER POWER OF ACTIVITY
00131 Y = FN * ACTSCL(NCONT + 1)           WWD1441
C   IF OUT OF RANGE, SCALE UP
00000 IF ACCUMULATOR OVERFLOW 161, 133   WWD1442
C                                           WWD1443
C   TRANSFER OUT TO CALCULATE PROPER MATRIX ELEMENTS FOR THIS POINT
00133 GO TO (601, 1001), NACIDS           WWD1444
C                                           WWD1445
C   RETURN FROM OBTAINING ELEMENTS, SET LOOP FOR NEXT POINT
C   SINGLE ACID
00135 K = K + 1                            WWD1446
C   TEST FOR LAST POINT USED. IF FINISHED, SOLVE MATRIX.
00137 IF (K - NDPTS) 801, 801, 701        WWD1447
C                                           WWD1448
C   RETURN FROM MATRIX SOLVE. OBTAIN DIFFERENCE FROM OLD ANSWERS
00139 SUM = 0.                             WWD1449
00141 DO 143 I = 1, NCON1                  WWD1450
00000 SUM = SUM + ABSF((RESULT(I) - CKPROD(I)) / RESULT(I)) WWD1451
C   REPLACE OLD ANSWERS WITH NEW
00143 CKPROD(I) = RESULT(I)               WWD1452
00000 CKIND(1) = RESULT(1)                WWD1453
00145 IF (NCON1 - 1) 904, 151, 147        WWD1454
00147 DO 149 I = 2, NCON1                 WWD1455
00149 CKIND(I) = RESULT(I) / RESULT(I - 1) WWD1456
C                                           WWD1457
C   WRITE ANSWERS AND DIFFERENCE FROM PREVIOUS SET
00151 WRITE OUTPUT TAPE 9, 72, (CKIND(I), I = 1, 4), SUM WWD1458
PUNCH 30, (CKIND(I), I = 1, 4), SUM      WWD1459
C   TEST FOR END. IF ANSWERS SATISFACTORY, OBTAIN STANDARD DEVIATIONS
00000 MCOUNT = MCOUNT + 1              WWD1460
153 IF (SUM - ERROR * FLOATF(NROWS)) 6001, 6001, 155 WWD1461
C                                           WWD1462
C   ANSWERS NOT GOOD ENOUGH. REPEAT IF NOT TOO MANY ITERATIONS
00155 MSCALE = 0                           WWD1463
00157 IF (MCOUNT - 10) 107, 6001, 6001    WWD1464
C                                           WWD1465
C   SCALE UP
C                                           WWD1466
C                                           WWD1467
C                                           WWD1468
C                                           WWD1469
C                                           WWD1470
C                                           WWD1471
C                                           WWD1472

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00161 IF (MSCALE) 905, 163, 163
00163 MSCALE = 1
00000 SCFTR = SCFTR + 1.
00000 GO TO 105
C
C      SCALE DOWN
00171 IF (MSCALE) 173, 173, 905
00173 MSCALE = -1
00000 SCFTR = SCFTR - 1.
00000 GO TO 105
C
C      TWO ACID, NON-LINEAR LEAST SQUARE SOLUTION
C
C      SET MEASURED VALUE
01001 FM(K) = Y
C      CALCULATE ELEMENTS FOR SIXTH CONSTANT, IF ANY
      1003 IF (CKPROD(6)) 1005, 1009, 1005
01005 DO 1007 I = 1, NCON1
00000 Z = I
00000 L = NCONT - 1 - I
01007 E(I+10) = ((Z * CACID1 + 2. * CACID2 - FN) * ACTSCL(L)) / (GAMMA(I) * GAMMA(6))
00000 E(6) = ((2. * CACID2 - FN) * ACTSCL(NCONT - 1)) / GAMMA(6)
00000 GO TO 1011
C      CALCULATE ELEMENTS FOR FIFTH CONSTANT, IF ANY
      1009 IF (CKPROD(5)) 1011, 1015, 1011
01011 DO 1013 I = 1, NCON1
00000 Z = I
00000 L = NCONT - I
01013 E(I+6) = ((Z * CACID1 + CACID2 - FN) * ACTSCL(L)) / (GAMMA(I) * GAMMA(5))
00000 E(5) = ((CACID2 - FN) * ACTSCL(NCONT)) / GAMMA(5)
C      CALCULATE ELEMENTS FOR FIRST ACID
01015 DO 1017 I = 1, NCON1
00000 Z = I
00000 L = NCONT + 1 - I
01017 E(I) = ((Z * CACID1 - FN) * ACTSCL(L)) / GAMMA(I)
C
C      OBTAIN DIFFERENTIAL ELEMENTS OF MATRIX
01019 IF ACCUMULATOR OVERFLOW 1021, 1021
01021 AR(K, 1) = E(1) + E(7) * CKPROD(5) + E(11) * CKPROD(6)
00000 AR(K, 2) = E(2) + E(8) * CKPROD(5) + E(12) * CKPROD(6)
00000 AR(K, 3) = E(3) + E(9) * CKPROD(5) + E(13) * CKPROD(6)
00000 AR(K, 4) = E(4) + E(10) * CKPROD(5) + E(14) * CKPROD(6)
00000 AR(K, NCON1+1) = E(5) + E(7) * CKPROD(1) + E(8) * CKPROD(2)
000001 + E(9) * CKPROD(3) + E(10) * CKPROD(4)
00000 AR(K, NCON1+2) = E(6) + E(11) * CKPROD(1) + E(12) * CKPROD(2)
000001 + E(13) * CKPROD(3) + E(14) * CKPROD(4)
C      CALCULATE FC
01023 FC(K) = CKPROD(1) * E(1) + CKPROD(2) * E(2) + CKPROD(3) * E(3) + CKPROD(4) *
010231 E(4) + CKPROD(5) * E(5) + CKPROD(6) * E(6) + CKPROD(1) * E(7) + CKPROD(5) *
010232 CKPROD(2) * E(8) + CKPROD(5) * CKPROD(3) * E(9) + CKPROD(5) * CKPROD(4) *
010233 E(10) + CKPROD(5) * CKPROD(1) * E(11) + CKPROD(6) * CKPROD(2) * E(12) *
010234 CKPROD(6) * CKPROD(3) * E(13) + CKPROD(6) * CKPROD(4) * E(14) + CKPROD(6)
00000 IF ACCUMULATOR OVERFLOW 161, 1025
C      SET LOOP FOR NEXT POINT
01025 K = K + 1
C      TEST FOR LAST POINT USED
01027 IF (K - NDPTS) 801, 801, 1380
C
C      MODIFIED AN E 208 PROGRAM
C
01380 DO 1430 J = 1, NDPTS
01430 DF(J) = FM(J) - FC(J)

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WWO1473
WWO1474
WWO1475
WWO1476
WWO1477
WWO1478
WWO1479
WWO1480
WWO1481
WWO1482
WWO1483
WWO1484
WWO1485
WWO1486
WWO1487
WWO1488
WWO1490
WWO1491
WWO1492
WWO1493
WWO1494
WWO1495
WWO1496
WWO1498
WWO1499
WWO1500
WWO1501
WWO1502
WWO1503
WWO1504
WWO1505
WWO1506
WWO1507
WWO1508
WWO1509
WWO1510
WWO1511
WWO1512
WWO1513
WWO1514
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WWO1534

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C      TESTING SWITCH FOR OPTIONAL OUTPUT
01450 IF (SENSE SWITCH 3) 1460, 1490
01460 DO 1480 J = 1, NDPTS
01480 WRITE OUTPUT TAPE 9, 74, (AR(J,K), K = 1, NCONT), DF(J)
C
C      CALCULATE
01490 DO 1520 L = 1, NCONT
01500 R(L, 1) = 0.
01510 DO 1520 J = 1, NDPTS
01520 R(L, 1) = R(L, 1) + AR(J, L) * DF(J)
01530 DO 1570 L = 1, NCONT
01540 DO 1570 K = 1, NCONT
01550 G(L, K) = 0.
01560 DO 1570 J = 1, NDPTS
01570 G(L,K) = G(L, K) + AR(J, L) * AR(J, K)
00000 IF ACCUMULATOR OVERFLOW 161, 1580
C      TEST SWITCH FOR R AND G OPTIONAL OUTPUT
01580 IF (SENSE SWITCH 4) 1590, 1600
01590 WRITE OUTPUT TAPE 9, 74, ((G(L,K), K=1,NCONT), R(L,1), L=1,NCONT)
C
C      IF G Y = R, THEN MATINV RETURNS WITH R REPLACED
C      BY Y AND G REPLACED BY G INVERSE
01600 MM = 1
01610 CALL MATINV (G, NCONT, R, MM, DETERM)
01615 GO TO (1620, 911, 1617), NTYPE1
01617 CKIND(1) = ACID1
00000 CKIND(2) = ACID2
00000 Q1 = 0.
00000 DO 1619 J = 1, NDPTS
01619 Q1 = Q1 + (DF(J) ** 2.)
00000 GO TO 1760
C
C      CHECK THE FIT
01620 Q1 = 0.
01625 DO 1630 J = 1, NDPTS
01630 Q1 = Q1 + (DF(J) ** 2.)
IF ACCUMULATOR OVERFLOW 161, 1635
01635 Q = ABSF(QOD - Q1)
01640 QOD = Q1
01645 LLD = LLD + 1
MCLLD = MCLLD + 1
C      IF FIT IS NOT GOOD ENOUGH, REPEAT IF NO. OF ITERATIONS IS
C      NOT TOO LARGE. CKPROD(J) CORRECTED IN ANY CASE
1650 DO 1653 J = 1, NCON1
1653 CKPROD(J) = CKPROD(J) + R(J,1)
IF (NCON2) 911, 1660, 1655
1655 DO 1659 J = 1, NCON2
1657 JJ = J + NCON1
1659 CKPROD(J + 4) = CKPROD(J + 4) + R(JJ, 1)
01660 IF (Q - ERQD) 1680, 1680, 1665
01665 IF (LLD - NID) 1670, 1680, 1760
C      TEST SWITCH FOR Y AND G INVERSE, OPTIONAL OUTPUT
01670 IF (SENSE SWITCH 4) 1675, 1677
01675 WRITE OUTPUT TAPE 9, 74, ((G(L,K), K = 1, NCONT), R(L, 1),
1 L = 1, NCONT), (CKPROD(L2), L2 = 1, 6), Q1
01677 GO TO 107
C
C      REPLACE DISSOCIATION CONSTANTS AND TEST FOR CLOSENESS.
C      RECORRECT FOR ACTIVITY AND REITERATE IF NECESSARY
01680 SUM = 0.
01685 RESULT(1) = CKPROD(1)
01690 IF (NCON1 - 2) 1705, 1695, 1695

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01695 DO 1700 I = 2, NCON1                                WWD1587
01700 RESULT(I) = CKPROD(I) / CKPROD(I - 1)              WWD1588
01705 IF (NCON2 - 1) 1720, 1715, 1710                    WWD1589
    1710 RESULT(6) = CKPROD(6) / CKPROD(5)
    1715 RESULT(5) = CKPROD(5)
01720 DO 1730 I = 1, 6                                    WWD1592
    IF (CKIND(I)) 914, 1730, 1725
01725 SUM = SUM + ABSF((RESULT(I) - CKIND(I)) / CKIND(I)) WWD1593
    1727 CKIND(I) = RESULT(I)
    1730 CONTINUE
00000 WRITE OUTPUT TAPE 9, 97, (CKIND(I), I = 1, 6), SUM WWD159
    PUNCH 30, (CKIND(I), I = 1, 6)
01735 IF (SUM - ERROR * FLOATF(NCONT)) 1760, 1760, 1740 WWD1596
01740 MSCALE = 0                                           WWD1597
01745 MCOUNT = MCOUNT + 1                               WWD1598
01750 IF (MCOUNT - 10) 107, 1760, 1760                    WWD1599
C                                                         WWD1600
C   CALCULATE THE CORRELATION MATRIX                       WWD1601
01760 DO 1770 J = 1, NCONT                                WWD1602
01765 DO 1770 K = 1, NCONT                                WWD1603
01770 U(J, K) = G(J, K) / SQRTF( G(J, J) * G(K, K) )     WWD1604
01775 DO 1780 L = 1, NCONT                                WWD1605
01780 U(L, L) = SQRTF( G(L, L) * Q1 / FLOATF(NDPTS - NCONT - 1) ) WWD1606
C
C   WRITE FINAL RESULTS
01785 WRITE OUTPUT TAPE 9, 76, Q1, MCLLD, ACTSCL(1)
01790 WRITE OUTPUT TAPE 9, 78                                WWD1609
01795 WRITE OUTPUT TAPE 9, 80, (J, CKIND(J), U(J,J), J = 1, 6) WWD1610
01800 WRITE OUTPUT TAPE 9, 82                                WWD1611
01810 DO 1820 L = 1, NCONT                                WWD1612
01820 WRITE OUTPUT TAPE 9, 84, (U(L,K), K = 1, NCONT)     WWD1613
01830 WRITE OUTPUT TAPE 9, 86                                WWD1614
01840 WRITE OUTPUT TAPE 9, 88, (TNTML(J), PH(J), CMU(J), ACTCFH(J), WWD1615
018401 FM(J), FC(J), DF(J), J = 1, NDPTS)                 WWD1616
00000 GO TO 401                                             WWD1617
C                                                         WWD1618
C   SUBMASTER PROGRAM FOR CALCULATION OF TITRATION CURVE
C                                                         WWD1620
C   READ LIMITS OF PH AND STEPPING INTERVAL
00201 READ 90, PHLOWR, PHUPPR, PHSTEP                       WWD1621
    WRITE OUTPUT TAPE 9, 91
C   INITIAL CONDITIONS                                     WWD1622
00000 K = 1                                                 WWD1623
00000 CMU(1) = GMU                                           WWD1624
00000 TNTML(1) = 0.                                          WWD1625
00000 PH(1) = PHLOWR                                         WWD1626
C
C   SCALING FACTOR                                         WWD1627
00203 ACTSCL(1) = 1.0E30                                     WWD1628
C   IF TWO ACIDS, MOVE CONSTANTS OVER TO MAKE THEM CONSECUTIVE
00205 GO TO (801, 207), NACIDS                               WWD1629
00207 DO 209 I = 1, NCON2                                    WWD1631
00000 M = NCON1 + I                                          WWD1632
00209 CKPROD(M) = CKPROD(I + 4)                             WWD1633
C
C   GO TO ACTIVITY CORRECTION SECTION
00000 GO TO 801                                             WWD1634
C
C   RETURN AND TRANSFER ACCORDING TO TYPE OF TITRATION
00211 GO TO (217, 217, 213, 213), NTYPE9                  WWD1635
C
C   TITRATIONS OF BASE                                     WWD1636

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00213 DO 215 I = 1, 4                                WWD1637
00215 ACTSCL(I + 1) = ACTSCL(I) * OHACT(2)           WWD1638
00000 GO TO 221                                       WWD1639
C
C   TITRATIONS OF ACID                                WWD1640
00217 DO 216 I = 1, 4                                WWD1641
00219 ACTSCL(I + 1) = ACTSCL(I) * HYDACT(2)         WWD1642
C                                                     WWD1643
C   OBTAIN ELEMENTS OF EQUATION
00221 DO 223 I = 1, NCON1                             WWD1645
00000 Z = I                                           WWD1646
00223 E(I) = (HAION(1) * Z * ACTSCL(I)) / (GAMMA(I) * ACTSCL(I + 1)) WWD1647
00225 GO TO (231, 227), NACIDS                       WWD1648
00227 DO 229 I = 1, NCON2                             WWD1649
00000 Z = I                                           WWD1650
00000 L = NCON1 + I                                   WWD1651
00229 E(L) = (HAION(6) * Z * ACTSCL(I)) / (GAMMA(I + 4) * ACTSCL(I + 1)) WWD1652
C
C   TRANSFER ACCORDING TO TYPE OF TITRATION
00231 GO TO (245, 241, 237, 233), NTYPE9            WWD1653
C
C   TYPE 4 TITRATION, SALT OF BASE WITH BASE
00233 RQDNA = -HYDACT(2) / GHYDRO + COH + CLION      WWD1655
00000 DO 235 I = 1, NCONT                             WWD1656
00235 RQDNA = RQDNA - (E(I) * CKPROD(I))            WWD1657
00000 CMLTNT = (RQDNA - CNA) * (VOLT / BASEN)        WWD1658
00000 GO TO 249                                       WWD1659
C
C   TYPE 3 TITRATION, BASE WITH ACID
C   TYPE 3 TITRATION                                WWD1660
00237 RQDCL = HYDACT(2) / GHYDRO - COH              WWD1661
00000 DO 239 I = 1, NCONT                             WWD1662
00239 RQDCL = RQDCL + (E(I) * CKPROD(I))            WWD1663
00000 CMLTNT = (RQDCL - CLION) * (VOLT / BASEN)      WWD1664
00000 GO TO 249                                       WWD1665
C
C   TYPE 2 TITRATION, SALT OF ACID WITH ACID
C   TYPE 2 TITRATION                                WWD1666
00241 RQDCL = HYDACT(2) / GHYDRO + CNA - COH        WWD1667
00000 DO 243 I = 1, NCONT                             WWD1668
00243 RQDCL = RQDCL - (E(I) * CKPROD(I))            WWD1669
00000 CMLTNT = (RQDCL - CLION) * (VOLT / BASEN)      WWD1670
00000 GO TO 249                                       WWD1671
C
C   TYPE 1 TITRATION, ACID WITH BASE
C   TYPE 1 TITRATION                                WWD1672
00245 RQDNA = COH - HYDACT(2) / GHYDRO              WWD1673
00000 DO 247 I = 1, NCONT                             WWD1674
00247 RQDNA = RQDNA + (E(I) * CKPROD(I))            WWD1675
00000 CMLTNT = (RQDNA - CNA) * (VOLT / BASEN)        WWD1675A
249 CONTINUE                                         WWD1675B
C
C   ADD TITRANT AND TEST FOR LIMIT                    WWD1676
00251 INTML(1) = INTML(1) + CMLTNT                  WWD1677
      IF ((CMLTNT ** 2.) - 1.0E-6) 255, 255, 253
C   OPTIONAL OUTPUT
253 IF (SENSE SWITCH 2) 254, 803
254 WRITE OUTPUT TAPE 9, 92, INTML(1), PH(1), CMU(1), GHYDRO
      GO TO 803
00255 WRITE OUTPUT TAPE 9, 92, INTML(1), PH(1), CMU(1), GHYDRO WWD1679
C
C   DO NEXT POINT, IF ANY LEFT                        WWD1680

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00257 PH(1) = PH(1) + PHSTEP	WWD1681
00259 IF (PH(1) - PHUPPR) 801, 801, 261	
261 PUNCH 92, TNTML(1), PH(1), CMU(1), GHYDRO	
GO TO 401	
C	WWD1764
C SUBMASTER PROGRAM TO CALCULATE CONCENTRATIONS OF ACIDS	
C	WWD1766
C GO TO READ IN TITRATION CURVE	WWD1767
00301 GO TO 501	WWD1768
C	
C RETURN FROM READ IN. DETERMINE MATRIX SIZE	WWD1769
00303 NROWS = NACIDS	WWD1770
00000 NCOLMS = NROWS + 1	WWD1771
C	
C SET ITERATION COUNTER AND INITIAL SUM	WWD1772
00000 MCOUNT = 0	WWD1773
00000 SUM = 1.	WWD1774
C	
C CLEAR RESULTS AND ARRAY	WWD1775
00305 DO 307 I = 1, NROWS	WWD1776
00000 RESULT(I) = 0.	WWD1777
00000 E(I) = 0.	WWD1778
00000 DO 307 J = 1, NCOLMS	WWD1779
00307 AR(I, J) = 0.	WWD1780
C	
C INITIALIZE LOOP	WWD1781
00309 K = 1	WWD1782
00000 GO TO 801	WWD1783
C RETURN FROM GAMMA CALCULATOR AND BRANCH ON TITRATION TYPE	WWD1784
00311 GO TO (315, 315, 313, 313), NTYPE9	WWD1785
00313 FN = -1.	WWD1786
00000 GO TO 317	WWD1787
00315 FN = 1.	WWD1788
00317 Y = FN * (HYDACT(2)/GHYDRO + CNA - COH - CLION)	WWD1789
C	
C OBTAIN ELEMENTS OF MATRIX	
00319 VNUM1 = 0.	WWD1791
00000 DO 321 I = 1, NCON1	WWD1792
00000 Z = I	WWD1793
00321 VNUM1 = VNUM1 + Z * FACTOR(I)	WWD1794
00000 E(1) = VNUM1 * VOLC / DENOM1	WWD1795
00323 GO TO (328, 325), NACIDS	WWD1796
C ELEMENTS FOR SECOND ACID	WWD1797
00325 VNUM2 = 0.	WWD1798
00000 DO 327 I = 1, NCON2	WWD1799
00000 Z = I	WWD1800
00327 VNUM2 = VNUM2 + Z * FACTOR(I + 4)	WWD1801
00000 E(2) = VNUM2 * VOLC / DENOM2	WWD1802
C	
C SOLVE FOR ANSWERS OR ERRORS	WWD1803
00328 IF (SUM - 1.0E-6) 345, 345, 329	WWD1804
C	
C BUILD MATRIX	WWD1805
00329 DO 333 L = 1, NROWS	WWD1806
00000 AR(L, NCOLMS) = AR(L, NCOLMS) + E(L) * Y	WWD1807
00331 DO 333 M = 1, L	WWD1808
00333 AR(L, M) = AR(L, M) + E(L) * E(M)	WWD1809
00000 K = K + 1	WWD1810
00335 IF (K - NDPTS) 801, 801, 701	WWD1811
C	
C RETURN FROM MATRIX SOLVE	WWD1812
00337 SUM = ((ACID1 - RESULT(1)) / ACID1) ** 2.	WWD1813

00000 ACID1 = RESULT(1)	WWD1814
00339 GO TO (343, 341), NACIDS	WWD1815
00341 SUM = SUM + ((ACID2 - RESULT(2)) / ACID2) ** 2.	WWD1816
00000 ACID2 = RESULT(2)	WWD1817
00343 WRITE OUTPUT TAPE 9, 99, ACID1, ACID2, SUM	WWD1818
MCOUNT = MCOUNT + 1	
IF (MCOUNT - 10) 305, 344, 344	
344 SUM = -1.0E+10	
GO TO 309	
C	
C DETERMINE STANDARD DEVIATIONS. OBTAIN DIFFERENTIAL ELEMENTS	
00345 FM(K) = Y	WWD1821
00000 AR(K, 1) = E(1)	WWD1822
00000 AR(K, 2) = E(2)	WWD1823
00000 FC(K) = E(1) * CACID1 + E(2) * CACID2	WWD1824
00000 K = K + 1	WWD1825
C TEST FOR LAST POINT USED	WWD1826
00347 IF (K - NDPTS) 801, 801, 349	WWD1827
C	
C SET NUMBER OF UNKNOWNNS FOR ERROR TREATMENT	WWD1828
00349 NCONT = NACIDS	WWD1829
00000 NID = 0	WWD1830
00000 ERQD = 0.	WWD1831
00000 QOD = 0.	WWD1832
PUNCH 99, ACID1, ACID2, SUM	
00000 GO TO 1380	WWD1833
C	WWD1683
C READ IN TITRATION CURVE	WWD1684
C	WWD1685
00501 I = 1	WWD1686
00503 GO TO (505, 505, 507), NTYPE2	WWD1687
00505 GO TO (515, 515, 513), NTYPE3	WWD1688
00507 GO TO (511, 511, 509), NTYPE3	WWD1689
00509 READ 93, TNTML(I), PH(I), CMU(I), ACTCFH(I)	WWD1690
00000 GO TO 517	WWD1691
00511 READ 94, TNTML(I), PH(I), ACTCFH(I)	WWD1692
00000 GO TO 517	WWD1693
00513 READ 96, TNTML(I), PH(I), CMU(I)	WWD1694
00000 GO TO 517	WWD1695
00515 READ 98, TNTML(I), PH(I)	WWD1696
C	
C TEST FOR END AT PH OF ZERO	WWD1697
00517 IF (PH(I)) 907, 521, 519	WWD1698
C	
C READ NEXT POINT	WWD1699
00519 I = I + 1	WWD1700
00000 GO TO 503	WWD1701
C	
C COUNT NUMBER OF POINTS	WWD1702
00521 NDPTS = I - 1	WWD1703
00523 GO TO (103, 401, 303), NTYPE1	
C	
C FORMATION OF MATRIX	WWD1705
C	WWD1706
C OBTAIN ELEMENTS OF EQUATION	WWD1707
C	WWD1708
00601 DO 605 I = 1, NCON1	WWD1709
00000 Z = I	WWD1710
00000 L = NCON1 + 1 - I	WWD1711
00603 E(I) = (((Z * CACID1) - FN) / GAMMA(I)) * ACTSCL(L)	WWD1712
C IF OVERFLOW, SCALE UP	WWD1713
00000 IF ACCUMULATOR OVERFLOW 161, 605	

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00605 CONTINUE
C
C      BUILD MATRIX
00607 DO 615 L = 1, NROWS
00000 AR(L, NCOLMS) = AR(L, NCOLMS) + E(L) * Y
C      IF OVERFLOW, SCALE UP
00000 IF ACCUMULATOR OVERFLOW 161, 609
00609 DO 615 M = 1, L
00000 AR(L, M) = AR(L, M) + E(L) * E(M)
00000 IF ACCUMULATOR OVERFLOW 613, 615
C      DETERMINE WHETHER TO SCALE UP OR DOWN
00613 IF (ABS(E(L)) - 1.0) 161, 161, 171
00615 CONTINUE
00617 GO TO 135
C
C      SOLVE MATRIX
C
C      RESET TRIGGERS
00701 IF ACCUMULATOR OVERFLOW 703, 703
00703 J = NROWS - 1
00705 IF(J) 912, 707, 711
C      IF ONLY ONE ROW, SOLVE DIRECTLY
00707 RESULT(1) = AR(1, 2) / AR(1, 1)
00709 GO TO (139, 912, 337), NTYPE1
C
C      FILL OUT MATRIX
00711 DO 715 K = 2, NROWS
00000 M = K - 1
00713 DO 715 L = 1, M
00715 AR(L, K) = AR(K, L)
C      OPTIONAL OUTPUT
      IF (SENSE SWITCH 5) 716, 717
716 WRITE OUTPUT TAPE 9, 51, ((AR(K,L), L = 1, 5), K = 1, NROWS)
C
C      SOLVE BY TRIANGULARIZATION
717 DO 727 I = 1, J
00000 M = I + 1
00719 DO 727 K = M, NROWS
00000 FB = -AR(I, 1) / AR(K, 1)
00723 DO 727 L = I, NCOLMS
00000 AR(K, L) = FB * AR(K, L) + AR(I, L)
00000 IF ACCUMULATOR OVERFLOW 725, 727
00725 IF (FB - 1.0) 161, 161, 171
00727 CONTINUE
C      OPTIONAL OUTPUT
      IF (SENSE SWITCH 5) 728, 729
728 WRITE OUTPUT TAPE 9, 55, ((AR(K,L), L = 1, 5), K = 1, NROWS)
00729 DO 737 I = 1, NROWS
00000 SUM = 0.
00000 K = I - 1
00000 M = NCOLMS - I
00731 IF (K) 912, 737, 733
00733 DO 735 L = 1, K
00000 N = NCOLMS - L
00000 SUM = SUM + RESULT(N) * AR(M, N)
00000 IF ACCUMULATOR OVERFLOW 161, 735
00735 CONTINUE
00737 RESULT(M) = ( AR(M, NCOLMS) - SUM ) / AR(M, M)
00739 GO TO (139, 912, 337), NTYPE1
C
C      ACTIVITY CORRECTION SECTION.  THIS SECTION CALCULATES ACTIVITY
C      COEFFICIENTS, VOLUME CORRECTIONS, IONIC CONCENTRATIONS, IONIC

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C      STRENGTH, ETC.
C      THE SUBSCRIPT (K) IS SET OUTSIDE THIS SECTION FOR THE POINT UNDER
C      CONSIDERATION.
C
C      OBTAIN HYDROGEN ION ACTIVITY OR CONCENTRATION AT THIS POINT
00801 HYDACT(2) = 10. ** (-PH(K))
C
C      RESET OVERFLOW TRIGGER
00000 IF ACCUMULATOR OVERFLOW 803, 803
C
C      TRANSFER DEPENDING UPON WHETHER OR NOT ACTIVITY CORRECTIONS ARE TO
C      BE MADE.
00803 GO TO (809, 805, 809), NTYPE2
C
C      NO CORRECTIONS. ALL ACTIVITIES EQUAL ONE
00805 GHYDRO = 1.
00000 ACTCFH(K) = 1.
00000 GOXIDE = 1.
00000 DO 807 I = 1, 6
00807 GAMMA(I) = 1.
00000 GO TO 835
C
C      ACTIVITY CORRECTIONS MADE. D-H FACTORS COMPUTED
00809 SRMU = SQRTF(CMU(K))
00000 ASRMU = -DBHFA * SRMU
00000 BSRMU = DBHFB * SRMU
00000 BETAML = BETADH * CMU(K)
C
C      ACTIVITY COEFFICIENTS FOR HYDROGEN AND HYDROXIDE IONS
C      IF HYDROGEN ACTIVITY READ IN, DO NOT CALCULATE
00811 GO TO (815, 903, 813), NTYPE2
00813 GHYDRO = ACTCFH(K)
00000 GO TO 817
00815 GHYDRO = 10. ** (ASRMU / (1. + BSRMU * HIONSZ) - BETAMU)
00000 ACTCFH(K) = GHYDRO
00817 GOXIDE = 10. ** (ASRMU / (1. + BSRMU * 3.5) - BETAMU)
C
C      ACTIVITY COEFFICIENTS FOR IONS OF FIRST ACID
00819 DO 821 I = 1, NCON1
00000 Z = I * I
00821 GAMMA(I) = 10. ** (ASRMU * Z / (1. + BSRMU * SIZION(I)) - BETAMU)
C
C      ACTIVITY COEFFICIENTS FOR IONS OF SECOND ACID
00823 GO TO (829, 825), NACIDS
00825 DO 827 I = 1, NCON2
00000 Z = I * I
00827 GAMMA(I+4) = 10. ** (ASRMU * Z / (1. + BSRMU * SIZION(I+4)) - BETAMU)
C
C      CORRECT VALUE OF HYDROGEN ACTIVITY FOR CALCULATING USE DEPENDING
C      UPON TYPE OF PH MEASUREMENT MADE.
00829 GO TO (835, 833, 831), NTYPE5
00831 HYDACT(2) = HYDACT(2) / GHYDRO
00000 GO TO 835
      833 HYDACT(2) = HYDACT(2) * GHYDRO
C
C      VOLUME CORRECTION SECTION
C      TEST FOR CONSTANT VOLUME
00835 GO TO (839, 837), NTYPE4
00837 VOLTL = SOLNV
00000 GO TO 841
C
C      CALCULATE TOTAL VOLUME

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00839 VOLTL = SOLNV + TNTML(K)                                WWD1304
C
C      HYDROXIDE ION CONCENTRATION                                WWD1305
00841 COH = WCON / (HYDACT(2) * GOXIDE)                          WWD1306
C
C      VOLUME CORRECTION FACTOR                                    WWD1307
00000 VOLC = SOLNV / VOLTL                                       WWD1308
C
C      CONCENTRATIONS OF ACIDS, CORRECTED                        WWD1309
00000 CACID1 = ACID1 * VOLC                                       WWD1310
00000 CACID2 = ACID2 * VOLC                                       WWD1311
C
C      BRANCH ACCORDING TO TYPE OF TITRATION                    WWD1312
00843 GO TO (867, 865, 847, 845), NTYPE9                          WWD1313
C
C      SALT OF BASE TITRATED WITH BASE                          WWD1314
00845 CNA = TNTML(K) * BASEN / VOLTL                             WWD1315
00000 CLION = CACID2 + CACID1                                       WWD1316
00000 GO TO 849                                                       WWD1317
C
C      BASE TITRATED WITH ACID                                   WWD1318
00847 CNA = 0.                                                       WWD1319
00000 CLION = TNTML(K) * BASEN / VOLTL                             WWD1320
C
C      POWERS OF HYDROXIDE ION ACTIVITY                         WWD1321
00849 OHACT(2) = WCON / HYDACT(2)                                    WWD1322
00000 OHACT(3) = OHACT(2) * OHACT(2)                               WWD1323
00000 OHACT(4) = OHACT(3) * OHACT(2)                               WWD1324
C
C      ERROR STOP IF PH OUT OF RANGE                             WWD1325
00000 IF ACCUMULATOR OVERFLOW 910, 850                          WWD1326
C
C      ION CONCENTRATION CALCULATION SECTION                    WWD1327
00850 IF QUOTIENT OVERFLOW 851, 851                                WWD1328
00851 DENOM1 = 1.                                                    WWD1329
00000 DO 853 I = 1, NCON1                                           WWD1330
00000 FACTOR(I) = CKPROD(I) / (GAMMA(I) * OHACT(I))               WWD1331
00000 FACTOR(I) = FACTOR(I) / OHACT(2)                             WWD1332
C
C      IF RESULT OUT OF RANGE, SET VALUE TO ZERO               WWD1333
00000 IF QUOTIENT OVERFLOW 852, 853                                WWD1334
00852 FACTOR(I) = 0.                                                WWD1335
00853 DENOM1 = DENOM1 + FACTOR(I)                                   WWD1336
C
C      CONCENTRATION OF UNIONIZED BASE NUMBER ONE              WWD1337
00000 HAION(1) = CACID1 / DENOM1                                    WWD1338
C
C      CONCENTRATION OF IONIC SPECIES                           WWD1339
00000 DO 855 I = 1, NCON1                                           WWD1340
00855 HAION(I + 1) = HAION(1) * FACTOR(I)                         WWD1341
00857 GO TO (885, 859), NACIDS                                       WWD1342
C
C      REPEAT ABOVE FOR SECOND BASE                             WWD1343
00859 DENOM2 = 1.                                                    WWD1344
00000 DO 861 I = 1, NCON2                                           WWD1345
00000 FACTOR(I+4) = CKPROD(I + 4) / (GAMMA(I + 4) * OHACT(I + 1)) WWD1346
00861 DENOM2 = DENOM2 + FACTOR(I + 4)                               WWD1347
00000 HAION(6) = CACID2 / DENOM2                                    WWD1348
00000 DO 863 I = 1, NCON2                                           WWD1349
00863 HAION(I + 6) = HAION(6) * FACTOR(I + 4)                     WWD1350
00000 GO TO 885                                                       WWD1351
C
C      TITRATION OF ACID SALT WITH ACID                        WWD1352
00865 CNA = CACID1 + CACID2                                         WWD1353
00000 CLION = TNTML(K) * BASEN / VOLTL                             WWD1354
00000 GO TO 869                                                       WWD1355
C
C      ACID TITRATED WITH BASE                                  WWD1356
00867 CNA = TNTML(K) * BASEN / VOLTL                             WWD1357

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00000 CLION = 0.
C POWERS OF HYDROGEN ION ACTIVITY
00869 HYDACT(3) = HYDACT(2) * HYDACT(2)
00000 HYDACT(4) = HYDACT(3) * HYDACT(2)
C ERROR STOP IF PH OUT OF RANGE
00000 IF ACCUMULATOR OVERFLOW 910, 870
C ION CONCENTRATION CALCULATION SECTION
00870 IF QUOTIENT OVERFLOW 871, 871
00871 DENOM1 = 1.
00000 DO 873 I = 1, NCON1
00000 FACTOR(I) = CKPROD(I) / (GAMMA(I) * HYDACT(I))
00000 FACTOR(I) = FACTOR(I) / HYDACT(2)
C IF RESULT OUT OF RANGE, SET VALUE TO ZERO
00000 IF QUOTIENT OVERFLOW 872, 873
00872 FACTOR(I) = 0.
00873 DENOM1 = DENOM1 + FACTOR(I)
C CONCENTRATION OF UNIONIZED ACID NUMBER ONE
00000 HAION(1) = CACID1 / DENOM1
C
C CONCENTRATION OF IONIC SPECIES
00000 DO 875 I = 1, NCON1
00875 HAION(I + 1) = HAION(1) * FACTOR(I)
00877 GO TO (885, 879), NACIDS
C REPEAT ABOVE FOR SECOND ACID
00879 DENOM2 = 1.
00000 DO 881 I = 1, NCON2
00000 FACTOR(I + 4) = CKPROD(I + 4) / (GAMMA(I + 4) * HYDACT(I + 1))
00881 DENOM2 = DENOM2 + FACTOR(I + 4)
00000 HAION(6) = CACID2 / DENOM2
00000 DO 883 I = 1, NCON2
00883 HAION(I + 6) = HAION(6) * FACTOR(I + 4)
C
C TRANSFER OUT IF NO ACTIVITY CORRECTIONS
00885 GO TO (887, 891, 887), NTYPE2
C TRANSFER OUT IF IONIC STRENGTH CONSTANT OR GIVEN AT EACH POINT
00887 GO TO (889, 891, 891), NTYPE3
C
C COMPUTE NEW IONIC STRENGTH
00889 CMU(K) = .5 * ( HYDACT(2)/GHYDRO + CNA + COH + CLION + HAION(2)
008891 + 4. * HAION(3) + 9. * HAION(4) + 16. * HAION(5) + HAION(7)
008892 + 4. * HAION(8) ) + (CKNO3 * VOLC)
C
C TRANSFER OUT TO PROPER SECTION OF MAIN PROGRAM. OUTPUT OPTIONAL.
891 IF (SENSE SWITCH 1) 893, 895
893 WRITE OUTPUT TAPE 9, 63, K, HYDACT(2), GHYDRO, CMU(K), VOLC,
1 (HAION(KS), KS = 1, 8)
895 GO TO (117, 211, 311), NTYPE1
C
C ERROR CALCULATION FOR DISSOCIATION CONSTANTS
C MUST SPECIFY TWO ACIDS TO ENTER NON-LINEAR TREATMENT AND CALCULATE
C STANDARD DEVIATIONS
C
06001 NACIDS = 2
00000 NID = 0
00000 ERQD = 0.
00000 QOD = 0.
00000 GO TO 107
C
C ERROR STOPS
C
00901 WRITE OUTPUT TAPE 9, 9010
GO TO 483

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WWD1359
 WWD1360
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 WWD1840
 WWD1841
 WWD1842
 WWD1843
 WWD1844

00902	WRITE OUTPUT TAPE 9, 9020	WWO1846
	GO TO 487	
00903	WRITE OUTPUT TAPE 9, 9030	WWO1848
	PUNCH 9030	
	PRINT 9080	
	STOP 33333	
00904	WRITE OUTPUT TAPE 9, 9040	WWO1850
	WRITE OUTPUT TAPE 9, 97, (CKIND(12), 12 = 1, 6), SUM	
00000	GO TO 401	WWO1851
00905	WRITE OUTPUT TAPE 9, 9050	WWO1852
00000	GO TO 401	WWO1853
00906	WRITE OUTPUT TAPE 9, 9060	WWO1854
00000	GO TO 401	WWO1855
00907	WRITE OUTPUT TAPE 9, 9070	WWO1856
	GO TO 503	
00909	WRITE OUTPUT TAPE 9, 9090	WWO1860
	NTYPE1 = 2	
	GO TO 501	
910	GO TO (920, 920, 930), NTYPE6	
920	WRITE OUTPUT TAPE 9, 9010	
	NTYPE6 = 3	
930	GO TO (135, 401, 940), NTYPE1	
940	K = K + 1	
	IF (SUM - 1.0E-6) 347, 347, 335	
00911	WRITE OUTPUT TAPE 9, 9110	WWO1864
	PUNCH 9110	
	PRINT 9080	
	STOP 33333	
00912	WRITE OUTPUT TAPE 9, 9120	WWO1866
00000	GO TO 401	WWO1867
913	WRITE OUTPUT TAPE 9, 9020	
	GO TO 4919	
914	WRITE OUTPUT TAPE 9, 9020	
	GO TO 1760	
C		
00008	FORMAT (92HIDUNNING DISSOCIATION CONSTANT CALCULATOR, TITRATION	WWO1027
00008	1URVE CRAWER, AND CONCENTRATION FINDER)	WWO1028
00010	FORMAT (72HO	WWO1029
000101)	WWO1030
00012	FORMAT (912)	WWO1031
00014	FORMAT (44HOTHIS PROGRAM CALCULATES ACID CONCENTRATIONS)	WWO1032
00016	FORMAT (42HOTHIS PROGRAM CALCULATES A TITRATION CURVE)	WWO1033
00018	FORMAT (47HOTHIS PROGRAM CALCULATES DISSOCIATION CONSTANTS)	WWO1034
00020	FORMAT (F8.5, F10.5)	WWO1035
00022	FORMAT (48HOORIGINAL ESTIMATES OF ACID CONCENTRATIONS ARE F9.6,	WWO1036
000221	8H AND F9.6, 8H MOLAR)	
00024	FORMAT (35HOORIGINAL ACID CONCENTRATIONS ARE F9.6,	WWO1038
000241	8H AND F9.6, 8H MOLAR)	
00026	FORMAT (F10.5, 3F10.7, E9.2, F6.1)	WWO1040
00028	FORMAT (25H INITIAL SOLUTION VOLUME F8.3, 19HML, TITRANT CONC.	WWO1041
000281	F7.4, 23HN, EST. IONIC STRENGTH F6.3, 18HMOLAR, ADDED SALT F6.3,	WWO1042
000282	6HMOLAR, / 32H DISSOCIATION CONSTANT OF WATER E9.2,	WWO1043
000283	28H, DESIRED CLOSENESS OF FIT F5.1, 16H PERCENT AVERAGE)	WWO1044
00030	FORMAT (6F10.3)	WWO1045
00032	FORMAT (47HOINITIAL VALUES OF DISSOCIATION CONSTANTS ARE 6E11.3)	WWO1046
00034	FORMAT (50HOINITIAL ESTIMATES OF DISSOCIATION CONSTANTS ARE	WWO1047
000341	6E11.3)	WWO1048
00036	FORMAT (33HONO ACTIVITY CORRECTIONS ARE MADE)	WWO1049
00038	FORMAT (F4.1, 5F5.1)	WWO1050
	40 FORMAT (25HOION SIZE PARAMETERS ARE 6F5.1)	
00042	FORMAT (32HOIONIC STRENGTH IS CONSTANT AT F6.3, 6H MOLAR)	WWO1052
00044	FORMAT (25HOVOLUME IS CONSTANT AT F8.3, 3H ML)	WWO1053

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00046 FORMAT (12HOPWH IS USED) WWD1054
00048 FORMAT (12HOPCH IS USED) WWD1055
00050 FORMAT (12HOPAH IS USED) WWD1056
51 FORMAT (50HOTHE FILLED OUT MATRIX, AFTER INSTRUCTION 715, IS /
1 ( 5E20.8 ))
00052 FORMAT (F4.1) WWD1057
00054 FORMAT (23H HYDROGEN ION SIZE IS F4.1) WWD1058
55 FORMAT (54HOTHE TRIANGULARIZED MATRIX, AFTER INSTRUCTION 727, IS /
1 ( 5E20.8 ))
00056 FORMAT (F8.5, F10.5) WWD1059
00058 FORMAT (26H D-H COEFFICIENTS ARE A= F8.5, 6H, B= F8.5) WWD1060
00060 FORMAT (F8.5) WWD1061
61 FORMAT (119HO K HYDACT GHYDRO ION.ST. VOLC HAION(1) HAIO
IN(2) HAION(3) HAION(4) HAION(5) HAION(6) HAION(7) HAION(8) )
00062 FORMAT (14H D-H BETA IS F8.5) WWD1062
63 FORMAT (1H I3, E11.2, F8.4, F9.5, F7.3, 8F10.6)
00064 FORMAT (32HOSALT OF BASE TITRATED WITH BASE) WWD1063
00066 FORMAT (24HOBASE TITRATED WITH ACID) WWD1064
00068 FORMAT (32HOSALT OF ACID TITRATED WITH ACID) WWD1065
70 FORMAT (24HOACID TITRATED WITH BASE)
00072 FORMAT (29HODISSOCIATION CONSTANTS ARE 4E11.3, WWD1067
000721 20H SUM OF SQUARES = F8.5) WWD1068
00074 FORMAT (1HO 8E14.7) WWD1069
76 FORMAT (4HOQ1=E16.8, 36H TOTAL NO. OF NON-LINEAR ITERATIONS= I4,
1 18H SCALING FACTOR= E8.1)
00078 FORMAT (42HO J FINAL CKIND(J) STANDARD DEVIATION ) WWD1071
00080 FORMAT (1H I3, E13.4, E22.8) WWD1072
00082 FORMAT (26HOTHE CORRELATION MATRIX IS) WWD1073
00084 FORMAT (1H 10E11.3) WWD1074
00086 FORMAT (83HOTITRANT ML PH IONIC STRENGTH H ACT COEF. FM(MEAS.) WWD1075
000861 FC(CALC.) DIFFERENCE )
00088 FORMAT(1H F8.3, F7.2, F11.6, F14.4, E14.3, 2E12.3) WWD1077
00090 FORMAT (F6.2, F10.2, F9.2) WWD1078
91 FORMAT (54HOTITRANT ML PH IONIC STRENGTH H ACT COEF.) WWD1079
92 FORMAT (1H F8.4, F12.3, F12.6, F19.4)
00093 FORMAT (F7.3, F10.3, F12.6, F8.4) WWD1081
00094 FORMAT (F7.3, F10.3, F10.4) WWD1082
00096 FORMAT (F7.3, F10.3, F12.6 ) WWD1083
00097 FORMAT (29HODISSOCIATION CONSTANTS ARE 6E11.3, WWD1084
000971 20H SUM OF SQUARES = F8.5 ) WWD1085
00098 FORMAT (F7.3, F10.3) WWD1086
99 FORMAT (9HOACID1 = F8.5, 13H M., ACID2 = F8.5,
1 22H M., SUM OF SQUARES = E11.4)
09010 FORMAT (73HOACID NUMBER TWO HAS NEGATIVE CONCENTRATION. ASSUME ONL
1Y ONE ACID PRESENT)
09020 FORMAT (30HOA CKIND OR CKPROD IS NEGATIVE ) WWD1089
09030 FORMAT (22HOWRONG TRANSFER IN 800 ) WWD1090
09040 FORMAT (34HOFIRST ACID HAS NO DISC. CONSTANTS) WWD1091
09050 FORMAT (38HOATTEMPTED TO SCALE IN BOTH DIRECTIONS ) WWD1092
09060 FORMAT (35HOOVERFLOW IN GETTING SCALING FACTOR ) WWD1093
09070 FORMAT (26HOA NEGATIVE PH ENCOUNTERED ) WWD1094
9080 FORMAT (45H IMPOSSIBLE ERROR STOP. DISCONTINUE PROGRAM.)
09090 FORMAT (20HOCKPROD OUT OF RANGE ) WWD1096
09100 FORMAT (28HOPH OUT OF RANGE, 849 OR 869 ) WWD1097
09110 FORMAT (23HOWRONG TRANSFER IN 1600 ) WWD1098
09120 FORMAT (22HOWRONG TRANSFER IN 700 ) WWD1099

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